CRITICAL ANALYSIS AND REVIEW OF FLASH POINTS OF HIGH MOLECULAR WEIGHT POLY-FUNCTIONAL C, H, N, O COMPOUNDS

A Thesis

by

DERRICK SCOTT THOMAS

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

May 2011

Major Subject: Chemical Engineering

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Approved by:

Co-Chairs of Committee,	Sam Mannan
	Carl Laird
Committee Member,	Eric Peterson
Head of Department,	Michael Pishko

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ABSTRACT

Critical Analysis and Review of Flash Points of High Molecular Weight Poly-functional C, H, N, O Compounds. (May 2011)

Derrick Scott Thomas, B. S., Texas A&M University

Co-Chairs of Advisory Committee: Dr. Sam Mannan
Dr. Carl Laird

The research focuses on the critical review and prediction of flash points of high molecular weight compounds used mainly in the specialty chemical area. Thus far this area of high molecular weight specialty chemicals has not been thoroughly reviewed for flash point prediction; therefore critical review for accuracy of experimental values is difficult. Without critical review, the chance of hazards occurring in the processing and handling of these compounds increases. A reliable method for making predictions is important to efficiently review experimental values since duplicate experimentation can be time consuming and costly.

Other research groups have shown that the flash point (FP) is strongly correlated to the normal boiling point (NBP), but experimental NBP is not feasible for chemicals of high molecular weight. The reliability of existing NBP prediction methods was found inadequate for the compounds analyzed in this work. Therefore, a new NBP prediction method was adopted first. This method is based on ten simple group contributions and the molecular weight of the molecule. The training set included 196 high molecular weight C, H, N and O compounds. It produced an average absolute error (AAE) of 13^{o}C, which is superior to any other model tested so far. An accurate NBP is essential for critical review and new method development for flash point. A preliminary data analysis based on chemical family analysis allowed for detection of

erroneous data points. These compounds were experimentally re-tested at a Huntsman facility. With a predicted normal boiling point, a new FP method that differentiates strong and weak hydrogen bonding compounds was developed. This was done because of the differences in entropy of vaporization for hydrogen bonding compounds. The training set consisted of 191 diverse C, H, N, O compounds ranging from 100 to 4,000 g/mol in molecular weight. The test set consisted of 97 compounds of similar diversity. Both data sets produced an AAE of 5^{o}C and maximum deviation of 17.5^{o}C.

It was also found that no substantial decomposition was found for these compounds at flash point conditions. These compounds appear to follow the same physical trends as lower molecular weight compounds. With this new method it is possible to critically review this class of chemicals as well as update NBP and other physical property data.

To my Lord and Savior Jesus Christ for giving me the enduring strength and ability to complete this research project

To my family for their continual support

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NOMENCLATURE

P	Pressure
T	Temperature
T_{avg}	Average temperature between the NBP and flash point
T_{NBP}	Temperature at the normal boiling point
T_b	Temperature at the normal boiling point
T_{FP}	Temperature at the flash point
T_L	Temperature at the lower flammability limit
T_U	Temperature at the upper flammability limit
LFL	Lower flammability limit
UFL	Upper flammability limit
P_{sat}	Saturation pressure
C_{st}	Stoichiometric fuel concentration needed to combust in air
M_w	Molecular weight
ΔH_{vap}	Enthalpy change or 'heat' of vaporization
ΔH_{NBP}	Enthalpy change or heat of vaporization at normal boiling point
ΔS_{vap}	Entropy change of vaporization
ΔS_{NBP}	Entropy change of vaporization at the normal boiling point
G	Gibbs free energy of the system
G^V	Gibbs free energy of the vapor phase of the system
G^L	Gibbs free energy of the liquid phase of the system
H	Enthalpy of the system
S	Entropy of the system

S^{L}	Entropy of the liquid phase of the system
S^{V}	Entropy of the vapor phase of the system
ΔS^{Trans}	Change of entropy of vaporization of translational freedom
ΔS^{Rot}	Change of entropy of vaporization of rotational freedom
ΔS^{Conf}	Change of entropy of vaporization of conformational freedom
β	Moles of oxygen needed for complete combustion

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INTRODUCTION AND MOTIVATION

The specialty chemical industry has been rapidly growing in recent times with the demand for high performing parts and equipment to supply the increasing level of technology. This increase in growth has led to rapid formulation, testing and manufacture of specialized intermediates and products. The specialty chemical industry also relies on quick product testing and production campaigns that are usually batch processes. Consequently these materials are handled, tested and sometimes processed without full knowledge of their physical properties and hazards which can lead to unforeseen, devastating consequences. It has also been found that current methods are not designed to accurately predict the experimental flash points of these high molecular weight compounds. A need has been identified to develop a method to quickly and accurately predict and update important chemical, physical and hazard properties of specialty materials before further handling, testing and processing is done. This work was directed toward the high molecular weight, organic poly-functional specialty materials; specifically those greater than 300 g/mole. This work specifically focused on the critical review and prediction of closed cup flash point values for those chemicals since physical testing can sometimes be time consuming and costly. With the increasing scrutiny of governmental legislation such as the European Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) initiative it will be economically beneficial for companies to have an efficient way to update and review physical and hazard properties for compliance.[1] It is important to have a method to review flash point values for detection of erroneous experimental values because of the hazards that can arise. For instance an over estimated value of flash point can result in process conditions that create a flammable environment. On the other hand an underestimated value may result in unnecessary

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This thesis follows the style of *Energy & Fuels.*

process restrictions and potential application potential that may be costly to a company. The analysis also was focused on the behavior of these materials at elevated temperatures to identify any anomalies such as decomposition that would depress the expected flash point value. Like any semi-empirical model, this method has a molecular weight range and functional group limitation that identify the boundaries of interpolation within the model. Extrapolation beyond the limits given in this work should be used with caution.

FLASH POINT AND LIMITS OF FLAMMABILITY

Definition and Purpose

Flash point is defined as the minimum temperature at which the vapor present over a liquid forms a flammable mixture when mixed with air. This is not to be confused with the 'fire point' which is the lowest temperature at which, on further heating beyond the flash point, the sample will support combustion for 5 seconds[2]. Flash point measurements of various types are used as one measure of the flammability of liquid materials. The flash point is also related to the lower flammability limit, which is the minimum concentration of the material in a combustible/air mixture that will produce a flame[2]. Figure 1 displays the interrelation of flammability properties graphically as they pertain to a compounds vapor pressure. Theoretically the lower flammability temperature and the flash point should be equivalent but due to differences in experimental procedures they are usually not the same.

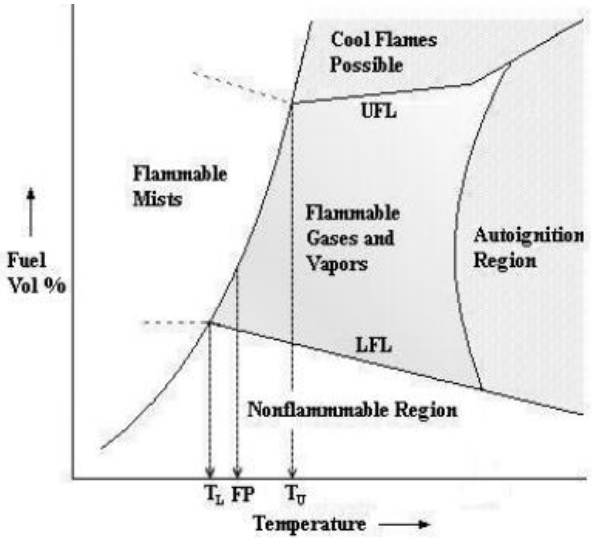

Figure 1 Flammability diagram for generic compound with vapor pressure curve[2]

Many manufacturing processes involve flammable chemicals; therefore, flash points and flammability limits are essential to maximize safety in process design and operational procedures. Flammability is an important factor in the development of safe practices for handling and storage of liquid mixtures. Regulatory agencies also use flash point determinations to classify flammable and combustible liquids in order to develop regulations such as those from EPA (Environmental Protection Agency) and DOT (Department of Transportation).

Flash Point Experimental Determination

According to J. Rowley[3], many attempts have been made to standardize the equipment for the experimental determination of flash points. In his work he mentions that the most widely used apparatuses include: Tag, Pensky-Martens, Cleveland, Setaflash and Abel. The first four apparatuses have been used in ASTM standardized methods for the flash point determination depending on the application, temperature range, and whether open or closed methods are required (Tag: D-56, D-1310 and D-3941; Pensky-Martens: D-93 and D-3941; Cleveland: D-92; and Setaflash: D-3278 and D-3828) [3].

The experimental flash point data used in this work is from closed cup apparatus tests. In closed cup determinations, the vapors are prevented to escape and they produce equilibrium conditions. The results obtained from this type of tests are usually few degrees lower than in an open cup test methods. The data used here come from either Pensky-Martens, or small scale (Setaflash) apparatus because they can handle the high temperature range required to test the substances studied in this work. Note that it has been reported that there is a systematic difference in the results for the same chemical when comparing the results obtained using the methods ASTM D-93, using a Pensky-Martens apparatus, and the ASTM D-3828, using a Setaflash apparatus (FP from Pensky-Martens are generally larger)[3]. Therefore, this difference has to be taken into account when comparing results from different methods. The flash point values for high molecular weight compounds reported in Huntsman's MSDSs were measured using a Penksy-Martens tester (see Figure 2). It is important that these values were accurate because the new semi-empirical flash point model extended to the high molecular weight region was mainly based on these values. In the following sections the flash point values are reviewed for accuracy based on known methods.

Figure 2 Pensky-Martens closed cup experimental apparatus used in this work

For the experimental testing using a Pensky-Martens, a liquid sample of 75 mL of each compound was loaded in the cup and the heater was set to a power setting allowing for a temperature increase of 5^{o}C/min. The sample was usually loaded at around 40 ^{o}C to allow for uniform mixing of the sample because of the tendency for some compounds to solidify at room temperature and air bubbles form in the liquid. It is also easier to pour at elevated temperatures. When the cup is locked in the heating bath, the stirrer is activated and the pilot light is ignited to test for ignition. The pilot light is lowered into the vapor space above the sample at every 0.5 ^{o}C change in temperature until a flash is observed. The mercury thermometer bulb was inserted half way down into the sample to obtain the most accurate temperature reading. The range of the thermometer was from 150 to 300 ^{o}C and the graduation on the thermometer was 0.5^{o}C. Table 1

shows the compounds tested using the Pensky-Martens closed cup tester at the Huntsman Advanced Technology Center. Some of these compounds were selected because analysis showed that their flash point value may be suspect as shown in section "*Flash Point Data Analysis*". These compounds were then used in the test set for the new flash point method. The "*Previous FP*" column shows the previous flash point value that was experimentally determined for that compound as shown on its MSDS. The "*New FP*" column displays the flash point value that was determined in this work. The apparatus was tested at 69.5 ^{o}C for calibration with a standard. It was also calibrated with reviewed values seen in the table and another compound at 130^{o}C. The purity of the samples was assumed to be between 98 and 99% by weight with heaviest impurity being water. From the MSDS for each compound the max weight percent of water is recorded with no compound having greater than 1% weight water. With the repeatability of the experimental method tested it is estimated that the accuracy of the new values shown in Table 1 is ± 2^{o}C.

Table 1 Experimental flash point tests in Pensky-Martin closed cup tester

Chemical Name	CAS #	Reference	Mw	Previous FP, ^{o}C	New FP, ^{o}C
SURFONIC L12-6*	66455-15-0	Huntsman MSDS	437	163	164.5
SURFONIC L12-8*	66455-15-0	Huntsman MSDS	525	173	175.5
SURFONIC TDA-8*	24938-91-8	Huntsman MSDS	553	176.7	178
PolyEthyleneGlycol-600	25322-68-3	Huntsman MSDS	616	210	214.5
Surfonic P-6	68987-81-5	Huntsman MSDS	1876	230	224
SURFONIC POA-L62	9003-11-6-	Huntsman MSDS	2193	235	225
JEFFOX WL 5000	9038-95-3	Huntsman MSDS	4108	225	237.5
Surfonic P-5	68551-13-3	Huntsman MSDS	769	246	229.5
Surfonic-T-15	61791-26-2	Huntsman MSDS	928	247	231
SURFONIC L24-22	9016-45-9	Huntsman MSDS	1168	253	233.5
Surfonic P-3	68551-13-3	Huntsman MSDS	632	234	214.5
SURFONIC LF-37	68154-97-2	Huntsman MSDS	1077	168	192
Surfonic T-10	61791-26-2	Huntsman MSDS	709	176	215
Surfonic OP-50	9036-19-5	Huntsman MSDS	426	224	188
Surfonic DA-6	78330-20-8	Huntsman MSDS	422	New	156
PolyEthyleneGlycol-1450	25322-68-3	Huntsman MSDS	1426	New	229
Surfonamine B-30	proprietary	Huntsman MSDS	321	290	160
XTJ-507	83713-01-3	Huntsman MSDS	2005	225	210
JEFFAMINE D-2000	9046-10-0	Huntsman MSDS	1988	225	210
Surfonic C-100	176022-81-4	Huntsman MSDS	1629	New	211

*Compounds used for calibration of flash point apparatus at higher temperatures

FLASH POINT PREDICTION METHODS LITERATURE REVIEW

Flash Point Estimation

Generally, the vapor pressure of compounds is a strong indicator of the rate and amount of evaporation: the lower the vapor pressure; the lower the evaporation. Flash point has a direct relation to evaporation and vapor pressure: the faster the evaporation rate, the lower the flash point. Therefore, there is a good relation between flash point and vapor pressure. Physically, the concentration of the chemical of interest in the vapor phase at the flash point can be modeled by the compounds vapor pressure at the temperature of the flash point. If the air and compound are assumed to be modeled by the ideal gas law then the equation below will apply.

$$\frac{P_{sat}(T_{FP})}{1\ atm} = mole\ fraction\ in\ vapor\ phase \tag{1}$$

According to Rowley[3,4] , models such as the one proposed by Leslie and Geniesse[5], which is based on this physical relationship between flash point and vapor pressure, have proven to be extremely accurate when used to predict flash point values for the 1062 chemicals reported in the DIPPR© 801 data base .

$$\frac{P_{sat}(T_{FP})}{1\ atm} = \frac{1}{8 \cdot \beta} \tag{2}$$

They found that there is a relationship between the vapor pressure at the flash point and the stoichiometric moles of oxygen, β, required to completely combust the material. The amount of

moles of oxygen needed to completely combust one mole of an organic molecule is described by the balanced chemical reaction equation given below[3],

$$C_xH_yO_zN_wS_vX_u + \beta O_2 \xrightarrow{yields} xCO_2 + \frac{y-u}{2}H_2O + \frac{w}{2}N_2 + vSO_2 + uHX \quad (3)$$

$$\beta = x + v + \frac{y-u}{4} - \frac{z}{2} \quad (4)$$

With this information known one can formulate a stoichiometric concentration of fuel in air needed for combustion.

$$C_{st} = \frac{1}{1 + 4.773 \cdot \beta} \quad (5)$$

Other methods have proposed a relationship to the molecular weight of the material instead of the stoichiometric moles of oxygen. However, it has been found that they are less accurate[3,4] and therefore, they are not discussed here. When accurate vapor pressure data is not available for the compound of interest, accurate estimation methods have been based on the normal boiling point, heat of vaporization and heat of combustion. The normal boiling point (NBP) provides the strongest correlation and NBP alone has proven to be an extremely accurate measure when families of molecules are used. Some accurate estimation methods based on NBP alone using linear and quadratic correlations have also proven to be quite accurate when using similar types of molecules but maximum deviations are often too large[6]. Some Quantitative-Structure Property Relationships (QSPR) methods even use the normal boiling point or an estimation of it in the formulation[7].

A compilation of methods for the determination of flash points, most of them based on the use of NBP, and their accuracy as applied to the DIPPR ® 801[8] data base of 1062 organic molecules can be found elsewhere (see ref. no. 3 for details). This database has a variety of chemicals containing C, H, N, O, P, halogen, S and Si atoms in their molecular structure. Therefore, it can be seen that the methods tested can handle a wide range of chemical classes. On the other hand, while QSPR and Neural Networks present a new class of modeling techniques that can be used for estimation of flash points, they still do not present any accuracy advantage over theoretically based methods using vapor pressure or normal boiling point[7,9,10].

Correlations trying to capture the flash point of all compounds without accurate vapor pressure measurements are difficult to achieve although extremely accurate correlations have been based on information about the NBP and the stoichiometric moles of oxygen with empirically fitted parameters. Methods such as the ones developed by Prugh[11], Catoire&Naudet[12], Ishuichi[13] and Rowley[3] have used such a correlation. The methodology used in this work is based on equation (1) which relates the flash point to the vapor pressure of the compound. Because experimental vapor pressure data or estimation methods is usually not readily available for high molecular weight poly-functional compounds, such as those examined in this work, an alternative method of estimation must be sought. Rowley[3] derived an equation (see equation 6) based on the *Leslie and Geinesse* flash point correlation[5] and the Clausius-Clapeyron vapor pressure approximation.

$$T_{FP} = \frac{T_{NBP}}{\frac{T_{NBP} * R * \ln(8 * \beta)}{\Delta H_{vap}} + 1} \qquad (6)$$

where, R is the universal gas constant 8.314 J/mol K, T_{NBP} is the NBP temperature (K), T_{FP} is the flash point temperature (K), β is the stoichiometric moles of oxygen needed for complete combustion, and ΔH_{vap} is the vaporization enthalpy between the two temperatures in J/mol. This equation was adopted in this work and is the basis for the model proposed.

On the other hand, from the data shown in Rowley's work about the average absolute deviation by estimation method for 1062 organic compounds in DIPPR® 801 database (see table 7.3 in '*Flammability Limits, Flash Points, and their Consanguinity: Critical Analysis, Experimental Exploration, and Prediction*' for details), it is evident that many methods using these properties, such as those proposed by Ishuichi[13], Catoire and Naudet[12] and Prugh[11] are more accurate than the equations based solely on normal boiling point for the diverse chemicals in the DIPPR© 801 data base. When testing those top performing models against the data sets shown in Appendix A, which include information from the DIPPR® 801 Database and Huntsman products, an interesting trend emerges, as seen in Figures 3 to 6. The methods incorporating normal boiling point and moles of oxygen tend to underestimate the flash point with increasing size of molecules. The methods using only NBP tend to overestimate the flash point with increasing molecular weight and boiling point. Both trends are dangerous if applied to a process but overestimation tends to cause a more hazardous environment. Basing the flash point solely on NBP tends to be more empirically based than coupling NBP with moles of oxygen so a more theoretical approach is favored. The origins of the deviations are explained in detail in section *Flash Point Method Development* of this thesis.

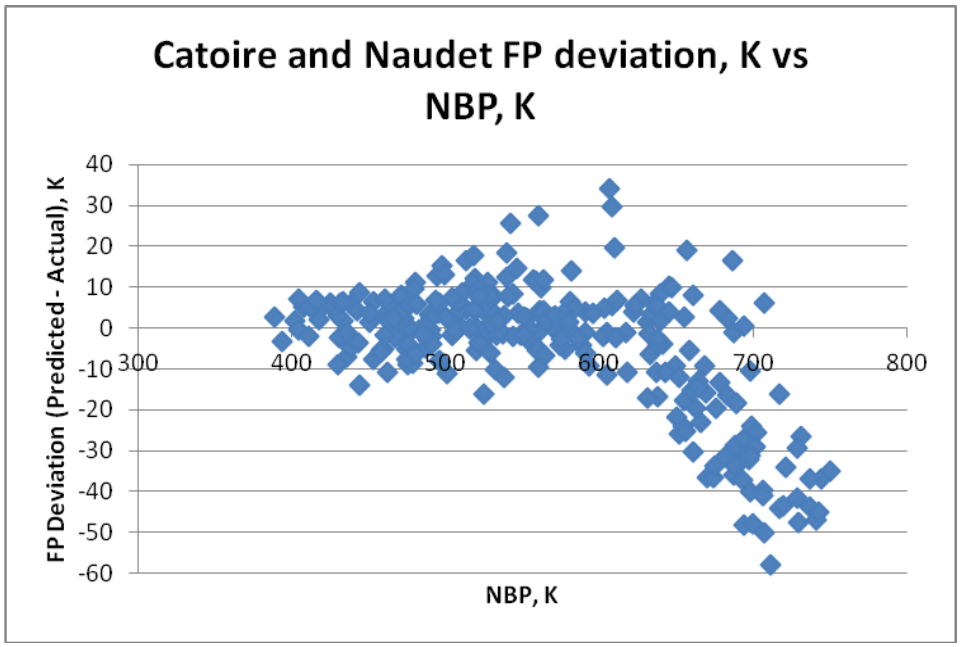

Figure 3 *Catoire and Naudet* prediction method behavior against Appendix A data sets

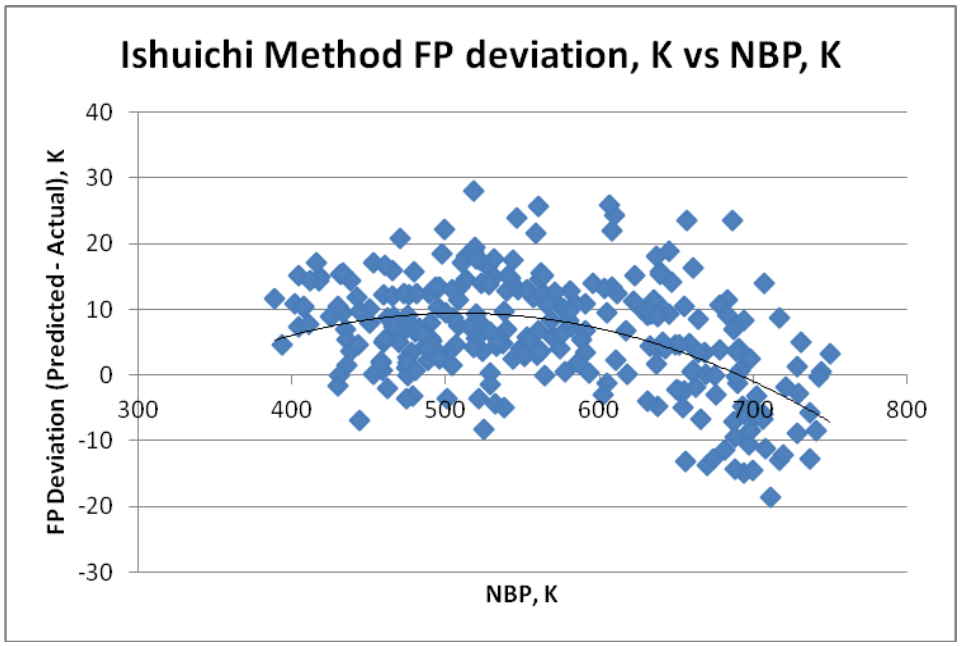

Figure 4 *Ishuichi* prediction method behavior against Appendix A data sets

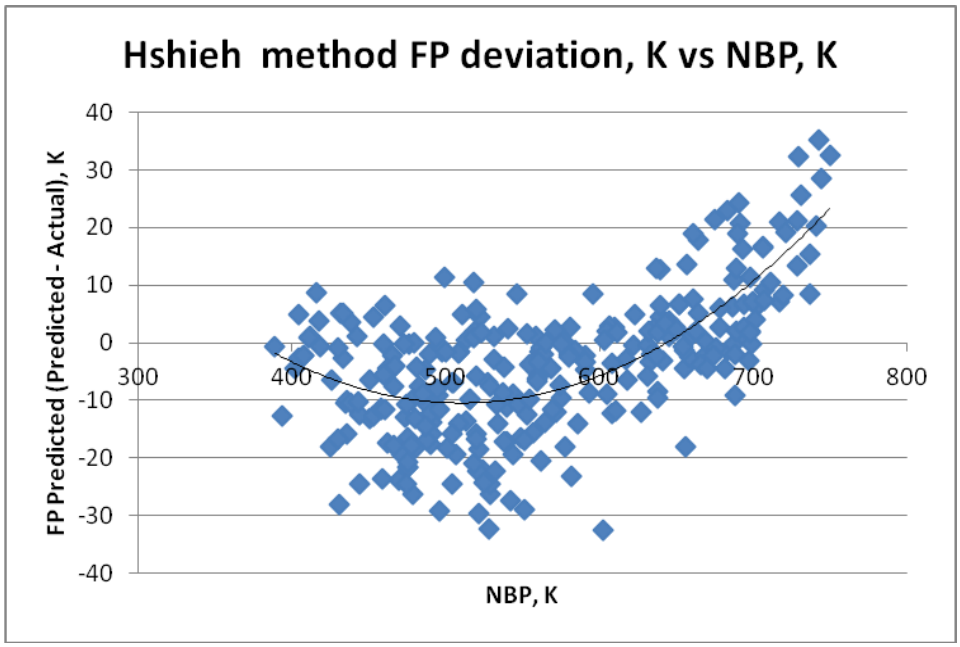

Figure 5 *Hshieh* prediction method behaviors against Appendix A data sets

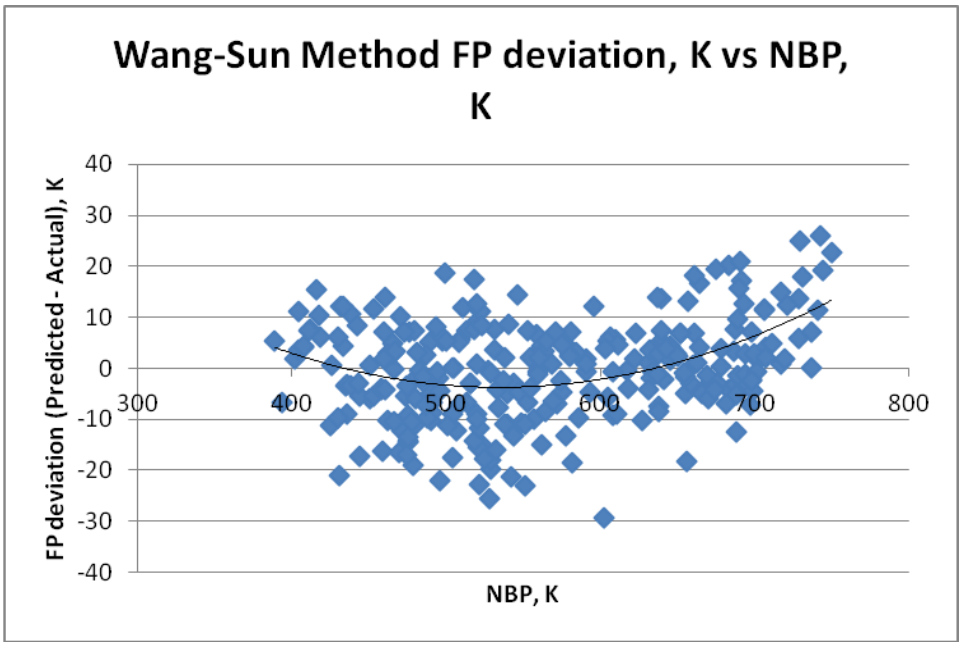

Figure 6 *Wang and Sun* prediction method behavior against Appendix A data sets

From the review of these existing flash point prediction methods it is evident that a new method is needed for the review of the compounds of high molecular weight, which are of interest in this work.

List of Existing Flash Point Estimation Methods

Leslie and Geniesse[6] observed that the vapor pressure at the flash point was an approximately constant function of stoichiometric moles of oxygen needed for combustion. *Rowley* found that although there is significant scatter about the fit proposed by *Leslie and Geniesse*, mainly for very small compounds, large errors in the vapor pressure correspond to small flash point errors[3]. See equation (2).

Catoire and Naudet[12] indentified a simple empirical equation for the estimation of closed-cup flash points for pure organic liquids. Data needed for the estimation of a flash point are the normal boiling point (T_{NBP}), the standard enthalpy of vaporization, $\Delta H_{vap}°$ (298.15 K) of the compound, and the number of carbon atoms (n) in the molecule. The same equation is shown to be valid for hydrocarbons, organic nitrogen compounds, organic oxygen compounds, organic sulfur compounds, organic halogen compounds, and organic silicone compounds. In addition, it seems that the flash points of organic deuterium compounds, organic tin compounds, organic nickel compounds, organic phosphorus compounds, organic boron compounds, and organic germanium compounds can also be predicted accurately by this equation.

$$T_{FP}(K) = 1.477 * {T_{NBP}}^{0.79686}(K) * {\Delta H^{\circ}_{vap}}^{0.16845} * n^{-0.05948} \qquad (7)$$

If no accurate data on enthalpy of vaporization at 298K is available then the following equation is recommended.

$$T_{FP}(K) = 0.3544 * {T_{NBP}}^{1.14711}(K) * n^{-0.07677} \quad (8)$$

The following section summarizes some other methods that have been used for the determination of flash points and that are relevant to this work. A more complete compilation of methods for the estimation of flash points can be found elsewhere (see ref. 3).

Prugh[11,3] developed a correlation for the estimation of the flash point for pure organic compounds based on the knowledge of their structure and normal boiling point.

$$T_{FP} = \frac{T_{NBP}}{a - b * \ln(C_{st})} \quad (9)$$

where, *a* and *b* are 1.3611 and 0.0697 for alcohols, and 1.442 and 0.08512 for other organic compounds respectively. 'C_{st}' is the stoichiometric concentration of fuel needed for complete combustion in air.

Ishiuchi[13,3] found a strong correlation with the flash point to the normal boiling point and stoichiometric moles of oxygen needed for complete combustion. In his work, it was concluded that there is an even stronger relationship when different parameters were used for associating compounds as opposed to non-associating compounds in the equation.

$$T_{FP}(K) = \left(T_{NBP}^{\alpha} + b * \left(\frac{\beta}{760}\right)^{-\alpha} + c\right)^{\frac{1}{\alpha}} \quad (10)$$

where, *a*, *b*, and *c* are 0.105, 0.0570, and 0.142 for associating chemicals, and 0.119, 0.0656, and 0.185 for all other compounds respectively.

Oehley[3,4] used the normal boiling point and chemical structure to estimate the flash point using the relationship shown below,

$$T_{FP}(K) = T_{NBP}(K) - 18 * \sqrt{4 * (n_C + n_S) + n_N + n_H - 2 * (n_O + n_{Cl}) - 3 * n_F - 5 * n_{Br}} \quad (11)$$

where, n_C, n_S, n_N, n_H, n_O, n_{Cl}, n_F, and n_{Br} are the number of atoms in the molecule of carbon, sulfur, nitrogen, oxygen, chlorine, fluorine and bromine, respectively.

Hshieh[14,3] found a correlation between the closed-cup flash point (^oC) of organic and silicon-containing compounds with the normal boiling point (^oC) and obtained

$$T_{FP} = a + b * T_{NBP} + c * T_{NBP}^2 \quad (12)$$

where, *a*, *b*, and *c* are -51.2385, 0.4994, and 0.00047, respectively, for silicon-containing compounds, and -54.5377, 0.5883, and 0.00022 for general organic compounds.

Wang and Sun[15, 3] found a linear relationship between the flash point of a diverse set organic compounds and the normal boiling point:

$$T_{FP}(K) = 57.6 + 0.64 * T_{NBP}(K) \quad (13)$$

FLASH POINT PREDICTION METHOD DEVELOPMENT

Flash Point Data Analysis

When developing semi-empirical prediction methods based on experimental data, it is always important to critically review the data to prevent the use of erroneous values. Compilation of data from databases is a useful resource. However, the quality and applicability of the data should be carefully assessed before making any conclusion. These considerations should take into account the conditions in which the data was obtained (*i.e.,* use of open or close methods); limitations of the experimental apparatus (*i.e.,* maximum/minimum temperature ranges); the potential use of safety margins in the reported values (*i.e.,* reporting the most conservative value); and adequate and complete documentation of all the parameters of interest. The last point is very important when deciding the use of a given data set. Incomplete documentation can lead to make assumptions that may be incorrect and may compromise the analysis of the selected data.

Most of the data presented in this thesis are from the DIPPR® 801 data base. The rest come from a compilation of data from Huntsman MSDS. The DIPPR® 801 database was used in this work because of its availability and because the quality of the data contained in this database. Before using the data from DIPPR® 801 database, a chemical series trend methodology was employed for the detection of erroneous values. This approach is one of the best ways to detect erroneous physical property and hazard data. The chemical series means using molecules with similar structure and functionality to develop trends for the property of interest analysis. It is known that normal boiling point is an excellent predictor of flash points especially of similar chemical classes[3,4,6,16]. This method is more accurate that a generalized equation but also far

more tedious. It is also not theoretically based, but more empirically founded on the data set used. These analyses have the added benefit of accurate predictions both for flash point and normal boiling point given one experimental value is available and the compound does not exhibit unusual behavior. Shown below, figures 7 and 8 show the chemical trend of the flash point as a function of normal boiling point for aromatic esters and various acid compounds from the DIPPR® 801 data base. The circled points show the values that are suspect and deviate from the predicted trend shown.

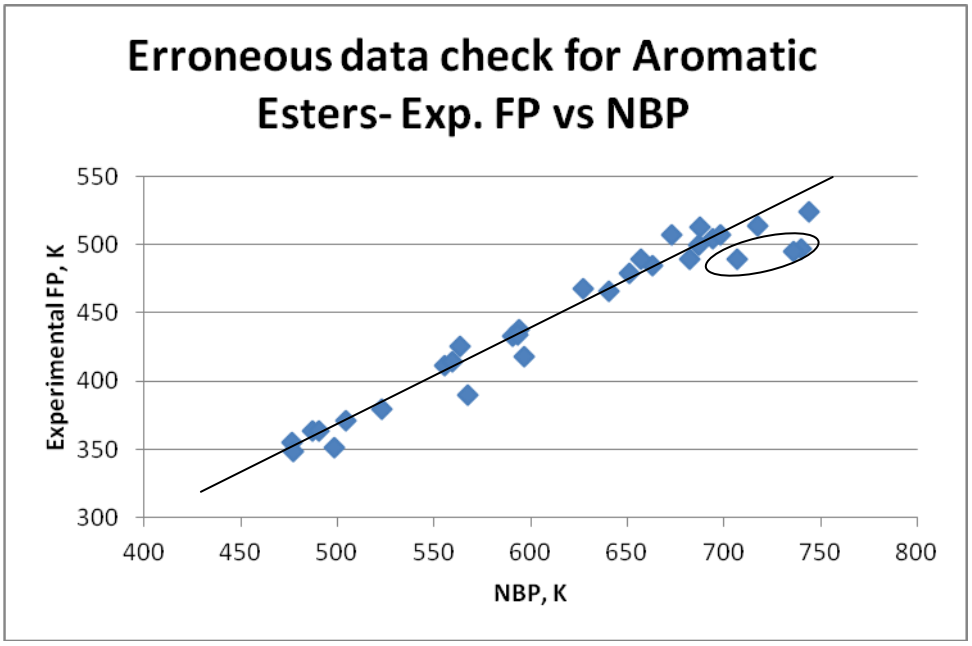

Figure 7 Erroneous flash point data check for aromatic esters

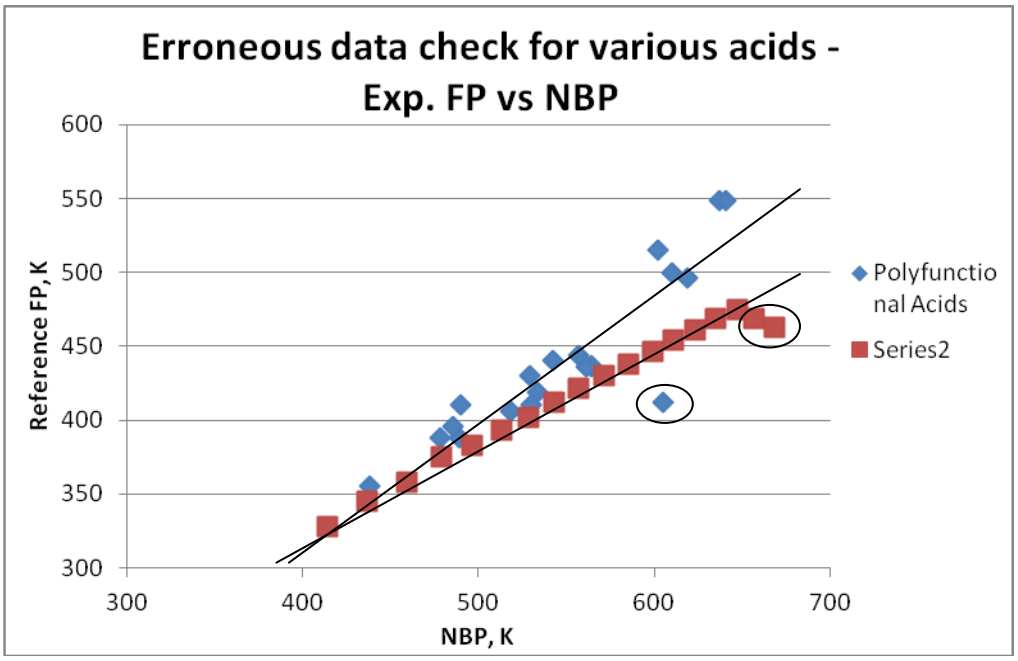

Figure 8 Erroneous flash point data check for regular and poly-functional acids

Similar plots in Figures 9-12 show the chemical trends of flash point as a function of normal boiling point for the higher molecular weight compounds. Again the circled points are those that were considered suspect and therefore recommended for re-evaluation or not used in the datasets. These graphs display a combination of DIPPR® 801 data base compounds and Huntsman Chemical specialty products. For the Huntsman products the closed cup flash point value was used from the MSDS or internal sources and the NBP was from the internal data base or estimated by the proposed method in this work.

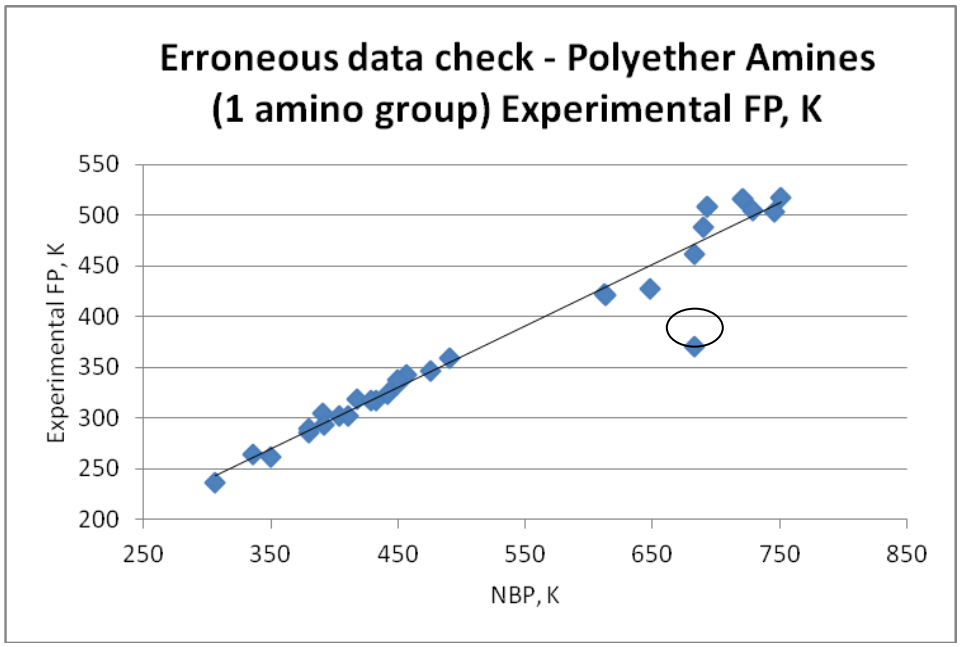

Figure 9 Erroneous flash point data check for polyether amines (1) amino group

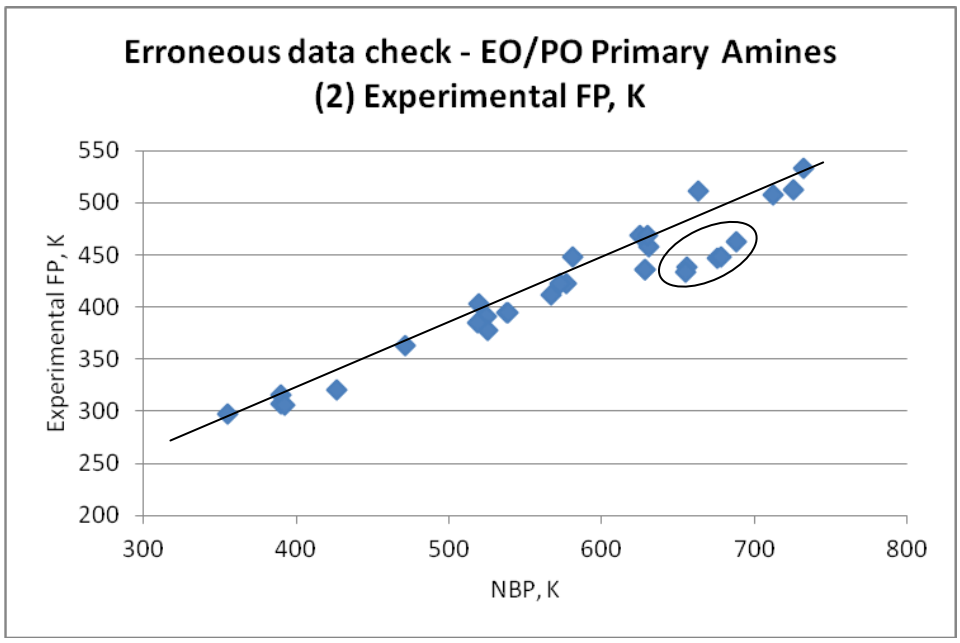

Figure 10 Erroneous flash point data check for polyether amines (2) amino groups

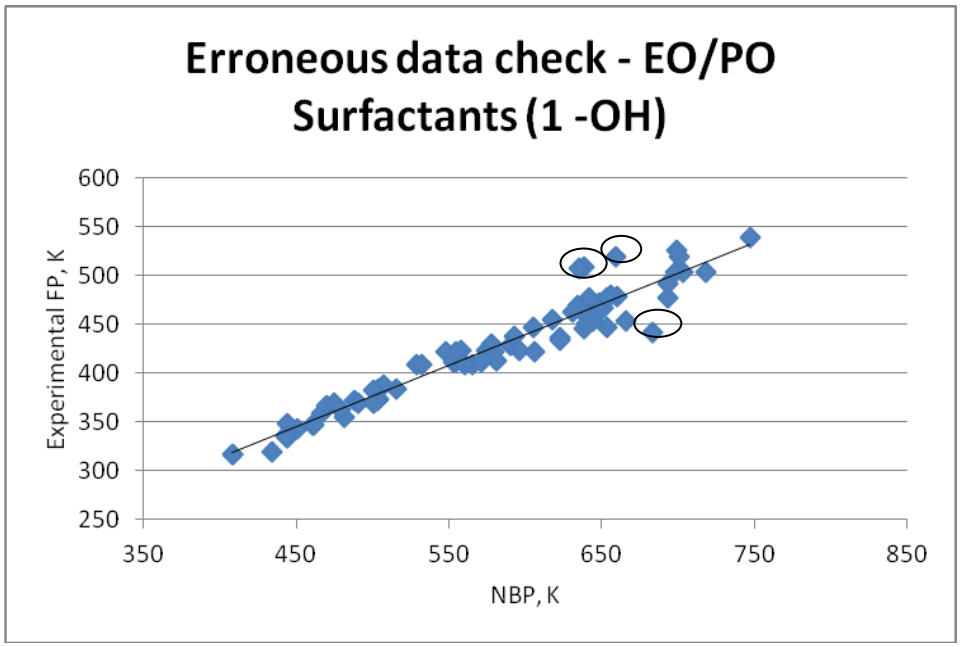

Figure 11 Erroneous flash point data check for polyether (1 –OH) surfactants

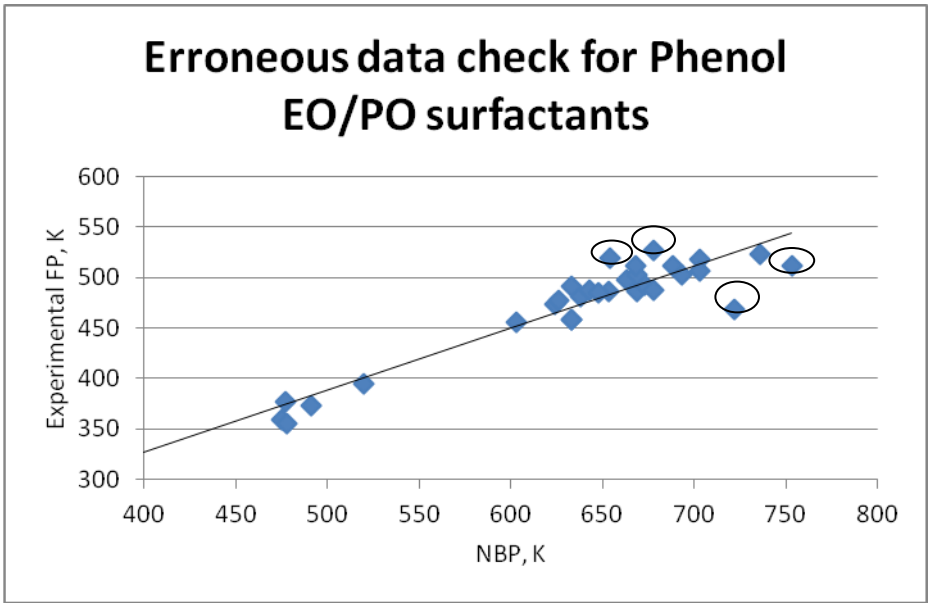

Figure 12 Erroneous flash point data check for polyether phenol surfactants

For the compounds that deviated from the trend, either the normal boiling point or the flash point data value was in error. Plots were also made of the flash point as a function of molecular weight but given the broad range of poly-functional chemicals used, it was difficult to spot outliers since molecular is not as strongly correlated to flash point as the normal boiling point. This method of checking for erroneous values was further supported by the fact that most of the compounds chosen for re-evaluation were indeed in significant error. It is evident by the changes in the selected chemicals chosen for re-evaluation by this method.

Compound Decomposition Review and Analysis

There was no substantial evidence of thermal decomposition of these compounds at the flash point temperature. Compounds of up to 4000 g/mol were used in this study and most followed the trends shown above, even trending with molecular weight. From "Pyrolysis of Polymers", studies conducted on the heat of vaporization of high molecular weight linear alkanes up to 1500-2150 g/mol were conducted at temperatures up to 345 ^{o}C with no observable amount of decomposition[17]. A study by DOW Chemical showed that thermal decomposition of their surfactants did not occur until 300 C in air[18]. A possible cause for some erroneous experimental tests for these types of compounds is contamination of the sample. Some samples in industry are kept for months and sometimes years in storage exposed to air and light. They can be used multiple times and contamination by impurities such as water and oxygen are likely to affect composition[19]. Future work should include a more extensive study on compound decomposition for these high molecular weight compounds. Methods such as liquid and gas chromatography on the samples and products to see if substantial decomposition has occurred at flash point conditions or above would give detailed description of such behavior.

Flash Point Prediction Method Development

In equation (6) the flash point is related to the NBP, heat of vaporization and stoichiometric moles of oxygen. When there is no accurate measure of the heat of vaporization at a specified temperature some methods have incorporated the well known *Trouton's rule* to estimate the ratio,

$$\frac{T_{NBP} * R}{\Delta H_{vap}} = \frac{1 * R}{\Delta S_{NBP}} \tag{14}$$

where, ΔS_{NBP} is the entropy of vaporization at the NBP. This vaporization entropy is estimated by Trouton as approximately 88 J*K−1*mol−1[20]. Unfortunately this method is not appropriate for molecules that exhibit hydrogen bonding and increasing rotational flexibility about bonds[20,21]. More accurate yet simple relationships have been developed to estimate the heats of vaporization by Trouton, Hildebrand, Everett[21] and Vetere[22]. They show that indeed the entropy of vaporization is not constant for all molecules but a non-linear logarithmic function of the normal boiling point. The method of Vetere[22] goes further to propose equations based on the molecular weight of the material. Since entropy is based on the randomness of the molecular configuration it only makes sense that the size of the molecule will play a role in the rotational degrees of freedom the molecule can have. Using this information the following equation is proposed in this work for the estimation of flash points;

$$T_{FP} = \frac{T_{NBP}}{\frac{\ln(8 * \beta)}{A + \mathbf{B} * \ln T_{NBP}} + \mathbf{1}} \tag{15}$$

This proved to be a more accurate fit of the experimental data than did assuming Trouton's constant to be valid. Even so, a better fit was found when molecular weight was included,

similar to that of the Vetere estimation methods, shown in equation (15). In *Pyrolysis of Polymers*, the authors report a non-linear function of molecular weight and temperature for high molecular weight linear carbon chains[17]. It was also noted that many flash point methods have separated their methods into categories of families of molecules. This is because of the polarity of certain functional groups and their tendencies to form hydrogen bonds. In this study, organic poly-functional C, H, N, O compounds are targeted for estimation and therefore use molecules of similar nature to make the estimation method more accurate. Even targeting molecules containing only C, H, N, O atoms there are still significant differences in behavior of these compounds. For example carboxylic acids, alcohols and primary/secondary amides form strong hydrogen bonds and require significantly more energy than hydrogen bonds formed by an amine group alone[23]. This has to do with the electro-negativity of the base molecule. The oxygen atom has higher electro-negativity than the nitrogen atom and therefore creates a stronger polar charge on the donor hydrogen molecule. It will also more strongly attract a donor hydrogen bonding atom[23]. The relevant bonds are those of oxygen with alcohol/amide groups and those of oxygen with amine groups. This arises because of the type of molecules used. Surfactants and resins contain ethylene oxide and propylene oxide groups in series. Thus an abundant source of oxygen atoms exists to form hydrogen bonds with the alcohol/amide and amine functional groups. Using these findings and the fact that other predictions methods used two separate equations for alcohol and non-alcohol containing compounds, it was decided to do the same. Therefore the final model will has unique parameters for -OH/amide and non-OH/amide containing compounds. A reliable fit was found by rearranging equation (6) in the form shown in equation (16) to view the behavior of the entropy of vaporization as a function of the compounds NBP and molecular weight as shown in Figure 8.

$$A(T_{NBP}, M_W) = \left(\frac{\frac{T_{NBP}}{T_{FP}} - 1}{\ln(8 * \beta)}\right)^{-1} = \frac{\Delta S_{vap}}{R} \tag{16}$$

Equation (17) is the model proposed for the flash points of high molecular weight C, H, N, O, and P organic compounds. The regression was first looked at in Excel by graphing the entropy of vaporization term against a logarithmic function of NBP and molecular weight, M_W, in grams per mol, and using the line of best fit. It was found that 'n' value of 0.5 and 1.25 are best for non-OH/amide and –OH/amide containing compounds respectively.

$$T_{FP} = \frac{T_{NBP}}{\frac{\ln(8 * \beta)}{A + B * \ln\left(\frac{T_{NBP}^{n}}{M_w}\right)} + 1} \tag{17}$$

The detailed regression was done in JMP® 8.0.2 statistical analysis software. The following figures show the regression statistics for the proposed model fit to the training set data.

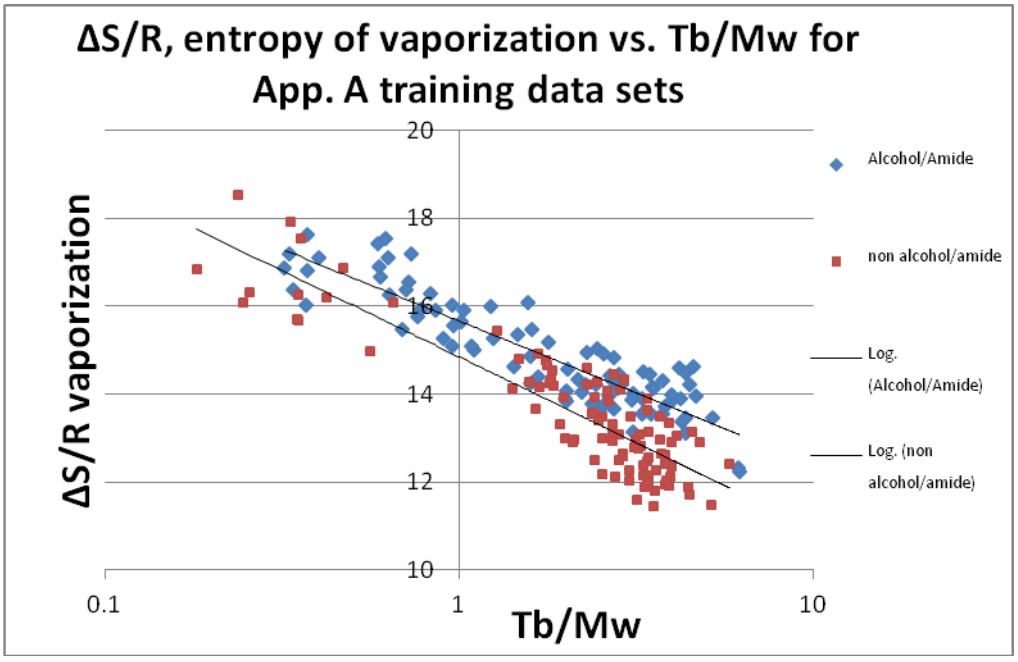

Figure 13 Analysis of vaporization enthalpy as a function of NBP and molecular weight

Figure 13 shows an analysis of the entropy of vaporiztion of both data sets as a function of the compounds normal boiling point and molecular weight on similar scales. As noted in the previous section it is verified that there is a statistical difference between the entropy of vaporization of alcohol/amide and non-alcohol/amide compounds. It is important to note that as the molecules get larger *i.e.*, higher molecular weight, the difference in entropy of vaporization becomes smaller. This makes sense physically that the larger the molecule becomes the more insignificant the hydrogen bonding becomes because of the amount of other interactions and conformations within the molecule[23].

Some statistical definitions used in the analysis below are presented here:

The ‘F-Ratio’ is the model mean square divided by the error mean square. The underlying hypothesis of the fit is that all the regression parameters (except the intercept) are zero. If this hypothesis is true, then both the mean square for error and the mean square for model estimate the error variance, and their ratio has an F-distribution. If a parameter has a significant model effect, the F-ratio is usually higher than expected by chance alone.

The ‘Prob > F’ is the observed significance probability (p-value) of obtaining a greater F-value by chance alone if the specified model fits no better than the overall response mean. Observed significance probabilities of 0.05 or less are often considered evidence of a regression effect.

The ‘t-Ratio’ lists the test statistics for the hypothesis that each parameter is zero. It is the ratio of the parameter estimate to its standard error. If the hypothesis is true, then this statistic has a t-distribution. Looking for a t-ratio greater than 2 in absolute value is a common rule of thumb for judging significance because it approximates the 0.05 significance level.

The ‘Prob>|t|’ lists the observed significance probability calculated from each t-ratio. It is the probability of getting, by chance alone, a t-ratio greater (in absolute value) than the computed value, given a true null hypothesis. Often, a value below 0.05 (or sometimes 0.01) is interpreted as evidence that the parameter is significantly different from zero.

The ‘R-Square’ measures the proportion of the variation around the mean explained by the linear or polynomial model. The remaining variation is not explained by the model and attributed to random error. R-square is 1 if the model fits perfectly. An R-square of 0 indicates that the fit is no better than the simple mean model.

Figure 14 shows the least squares regression of the parameters in equation 17 for alcohols/amide containing molecules. One can see the strong correlation between the variables from the R-squared value. The dashed lines encompassing the dark pink shaded area shows the 95% confidence interval for the line of best fit. The dashed lines encompassing the light pink shaded area shows the 95% confidence interval for indivdual predicted values using the prediction equation. In Figure 15 the residuals are distributed normally about the fit further strenghtening the ability of the model.

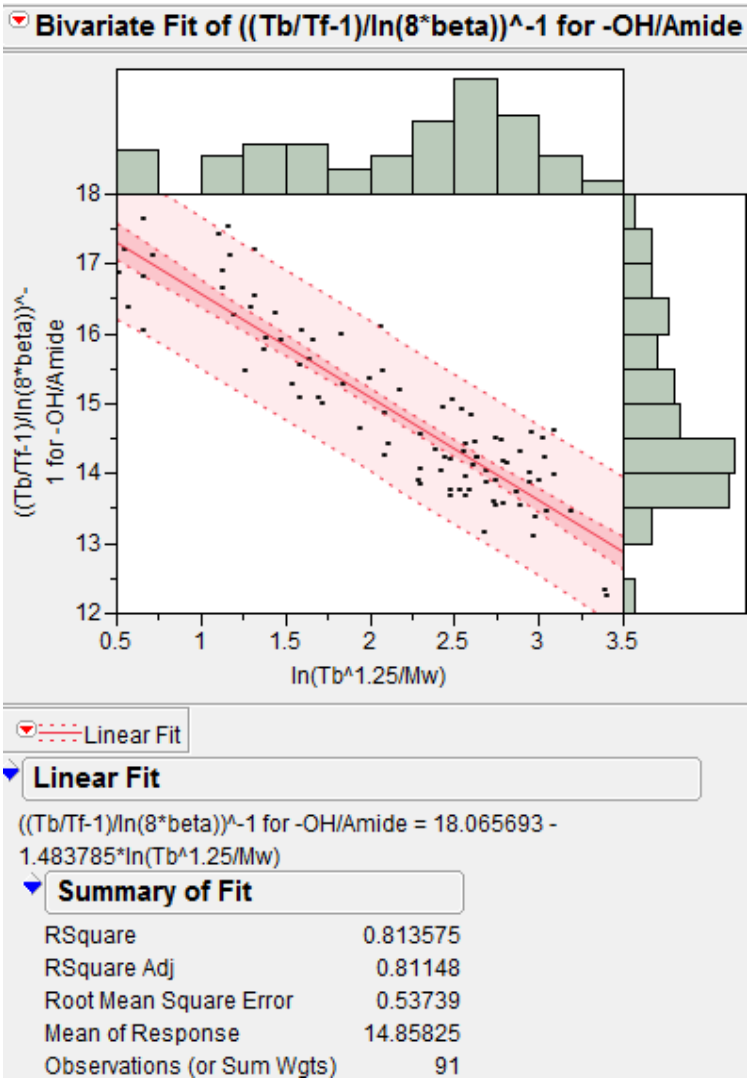

Figure 14 Statistical analysis of regression fit for –OH/Amide compounds

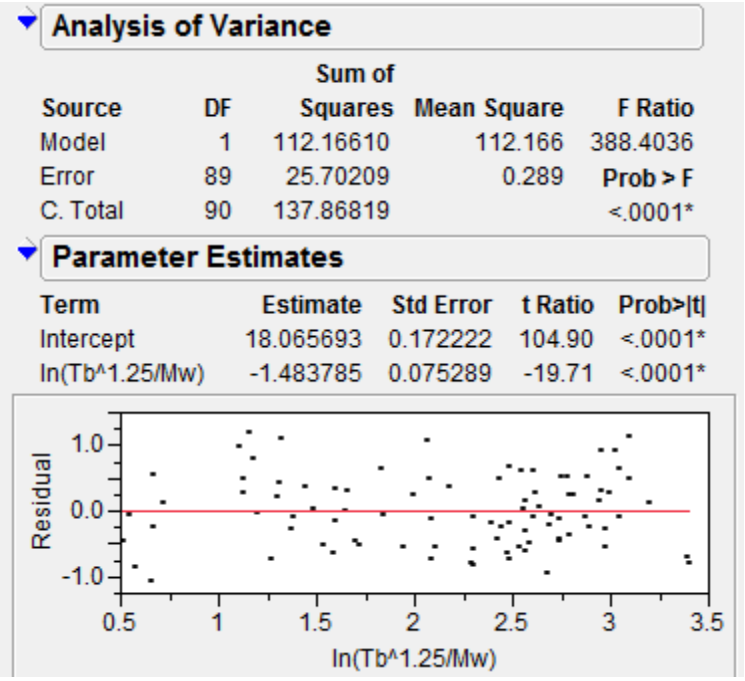

Figure 15 Analysis of variance and parameter correlation of fit –OH/Amide compounds

Figure 16 shows the least squares regression of the parameters in equation (17) for non-alcohols/amide containing molecules. Even though there is fewer data in the high molecular weight range, there is still a similarily strong correlation between the variables. It also follows the physical trend shown in Figure 14. In Figure 17 the residuals are distributed normally about the fit, again further strenghtensingthe ability of the model.

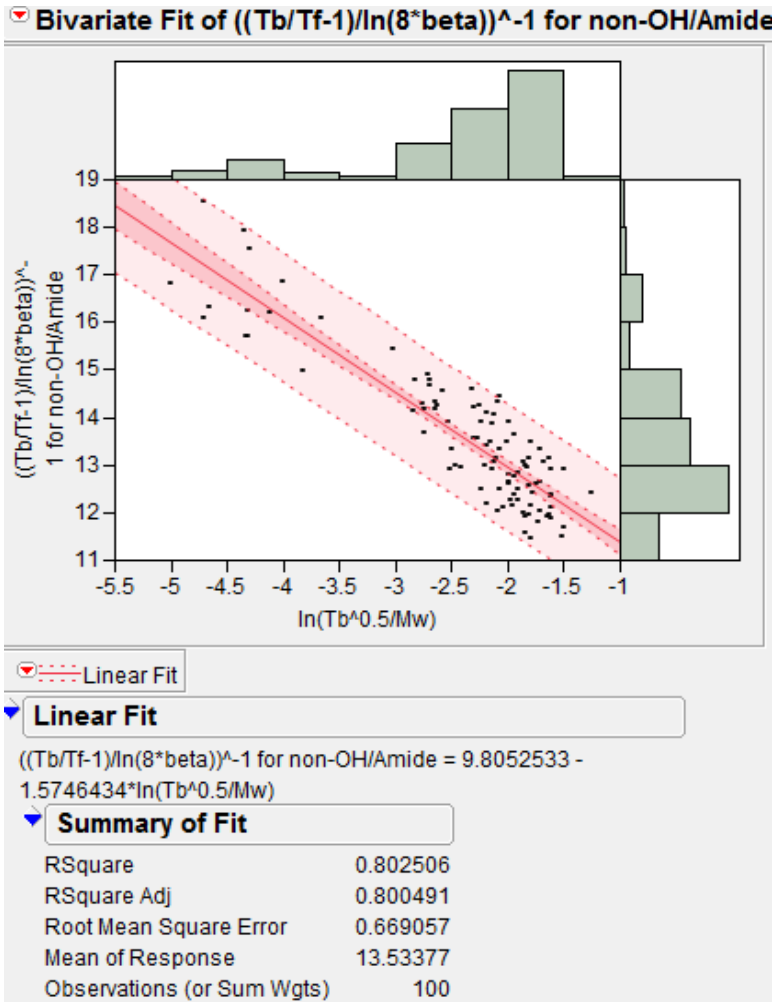

Figure 16 Statistical analysis of regression fit for non -OH/Amide compounds

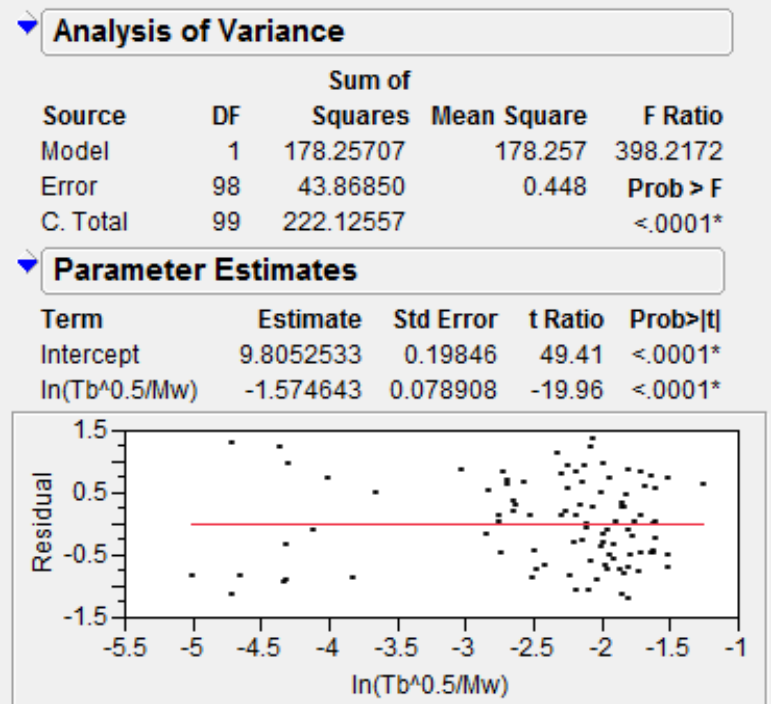

Figure 17 Analysis of variance and parameter correlation for non-OH/Amide compounds

The final models parameters for equation (17) are n=0.5, A=9.805 and B=-1.575 for non-alcohol containing molecules and n=1.25, A=18.066 and B=-1.484 for alcohol/amide containing molecules. From the analysis one should note that the larger compounds have higher entropy of vaporization. This validates theoretical and empirical evidence because of this quantity being the entropy of vaporization, it increases as the size and hydrogen bonding atoms increase in the molecule[17,21,22]. An analysis of this quantity in Table 2 shows that the minimum entropy of vaporization displayed by smaller molecules used in this work matches well to the base entropy of vaporization for smaller molecules calculated by Trouton's rule in equation (18).[20,21]

Table 2 Analysis of entropy of vaporization term of training set

Chemical Class	Avg M_W	Avg NBP	Avg ΔS_{vap}	Stdev ΔS_{vap}	Max ΔS_{vap}	Min ΔS_{vap}
Non –OH, amide	482.9	292.7	13.5	1.2	18.5	11.5
-OH, amide	510.4	310.7	14.5	1.9	17.7	12.2

$$\frac{\Delta H_{NBP}}{R * T_{NBP}} = \frac{\Delta S_{NBP}}{R} = 10.63 \quad (18)$$

Some differences between the two are a result of the inherent errors of the model. Errors are present because of the flaws in the Leslie and Geniesse method. The Clausius-Clapeyron equation also has physical assumptions that include the enthalpy of vaporization between the two temperatures being constant. Thus the enthalpy of vaporization will be an average of the two temperatures at which it is calculated. In the equation proposed it will be the boiling point temperature and the flash point temperature. This will undoubtedly produce error in the vapor pressure calculation and entropy of vaporization. Since it is known that the enthalpy of vaporization is greater at lower temperatures then the average heat of vaporization between the normal boiling point and flash point temperatures will be greater than at the normal boiling point alone.

$$\Delta H_{vap}(Prediction\ equation) = \Delta H_{vap}(T_{avg}) = \frac{(\Delta H_{vap}(T_{FP}) + \Delta H_{vap}(T_{NBP}))}{2} \quad (19)$$

$$\Delta H_{vap}(T_{FP}) > \Delta H_{vap}(T_{NBP}) \quad (20)$$

$$\Delta H_{vap}(T_{avg}) > \Delta H_{vap}(T_{NBP}) \quad (21)$$

Therefore,

$$\Delta S_{vap}(T_{avg}) > \Delta S_{vap}(T_{NBP}) \quad (22)$$

These errors may contribute to the increase in average entropy of vaporization as seen in the previous table. More analysis should be conducted to see how well this measure of entropy of vaporization measures to actual values at the normal boiling point or the flash point. The entropy of vaporization value in this model may be a potential method to accurately estimate enthalpy of vaporization at the normal boiling point or the flash point. Since the model is semi-empirical the accuracy and usability of the model will be dependent on the training set used to develop the coefficients. A semi-empirical model should always be used with caution with regards to the types of chemicals used, range of molecular weights and NBP range. The methods proposed in this study are geared toward high molecular weight range of C, H, N, O poly-functional compounds. Groups that were not used in the training set were nitro, nitrate, nitrile, imine, imid, pyridine, peroxide, sulfur, or halogen containing molecules. The model should only be used for those compounds which fit the range of application of the dataset. Three compounds were tested that had up to 4000 molecular weight so that should be the limit of the size of a compound used. The molecule should also have poly-functional characteristics with C, H, N, O atoms, with the exception of the functional groups listed above. The model should not be used on any compound with molecular weight less than 200 grams per mole because other models may fit better since their dataset is solely based on smaller compounds.

Propagation of Error and Regression Analysis

Since the flash point model uses experimental and predicted data in the regression training set, propagation of error is possible due to uncertainty of predictions and experimental data. Due to the time and effort it would have taken to assess and include the propagation of error for each data point included in the model, this analysis was not done. The fact that the model uses both experimental normal boiling points as well as predicted NBP in the regression training complicates the issue even more. The flash point data points also come from many different data sources with some of unknown experimental error. Figure 18 displays the sources of error propagation that could possibly accumulate in the development of the flash point model for high molecular weight compounds.

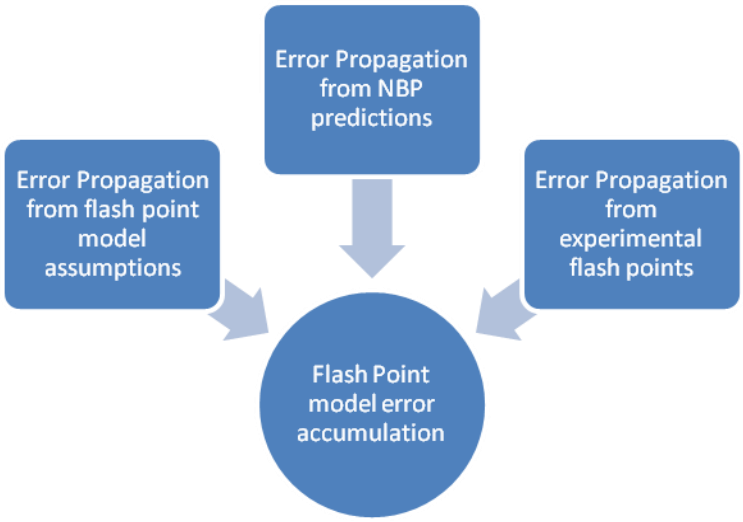

Figure 18 Overview of possible error propagation involved in flash point model development

To try and alleviate the effect of error propagation, the flash point model incorporates a somewhat evenly distribution of molecular weights so as not to allow a few data points to dictate the regression model. The statistical software JMP®8.0.2 allowed for detection of high leverage data points used in the regression training sets. Since least squares regression was used there is potential for high leverage points to influence the best fit model. This analysis of high leverage points showed no evidence that any points substantially influenced the regressed parameters. There was also an effort to try and understand the propagation of error by analyzing the data used in the flash point regression training set separately, *i.e.,* those that use experimental NBP and those that use predicted NBP by the method proposed in this work. See Figures 18 and 20 in the next section for further details. In addition the confidence intervals and error analysis for the NBP prediction method is assessed in the section *Normal Boiling Point Method Analysis and Comparisons* and the experimental error for the Huntsman compounds are given in the experimental section. With these analyses one can gain an idea of how much error propagation is possible in the flash point model and the accuracy of the prediction model.

Flash Point Prediction Method Analysis and Comparisons

The following section details the comparison of the statistical accuracy of proven methods versus the new model of the data sets in appendix A. Flash point models were chosen from Table 5 based on the accuracy and available inputs from the data sets. From Table 3 and 4 one can see that the new method is superior to the other proven methods. It is important to note the most accurate methods of Wang-Sun[16] and Ishuichi[14] and their model development characteristics. The Wang-Sun method is based on poly-functional organic molecules using

topological indices. The model is based solely on the normal boiling point with a linear fit of two correlation coefficients to regression data set. The authors report an average error of 3.5% for 1470 organic compounds[16]. The Ishuichi method is based on poly-functional organic molecules with flash points and normal boiling points up to 300 ^{o}C and 500 ^{o}C respectively and up to 20 carbons in size[14]. Their model is based on the normal boiling point and stoichiometric moles of oxygen needed for complete combustion with three correlation coefficients with the NBP being the strongest correlative variable. Based on the accuracy and maximum deviations of the top performing models they would not be reliable for accurate predictions of the flash points of high molecular weight poly-functional compounds[7]. For the method proposed in this paper with a absolute deviation of 5.0 ^{o}C and maximum deviation of around 17.5 ^{o}C it is acceptable for prediction of compounds that fit in the range of applicability given.

Figure 19 shows the fit of the experimental flash point values vs. the predicted values of the method proposed. The fit is broken down into four groups. Two groups use an experimental NBP from selected data base sources while the other two groups are those compounds that have an estimated NBP from the method proposed in this work. The Figure shows the 95% confidence intervals for the predicted values based on the level of certainty of the NBP. It will increase the max deviations up to 20 ^{o}C for the predicted flash point values of higher molecular weight compounds using this method. It is still evident that the fit is extremely strong for the full range of data with an R^2 value of 0.99. Table 2 and Figure 20 show some statistics of the characteristics of the compounds used in this study. From the review conducted in this study, the classes and sizes of compounds used here have not been previously reported in any other study.

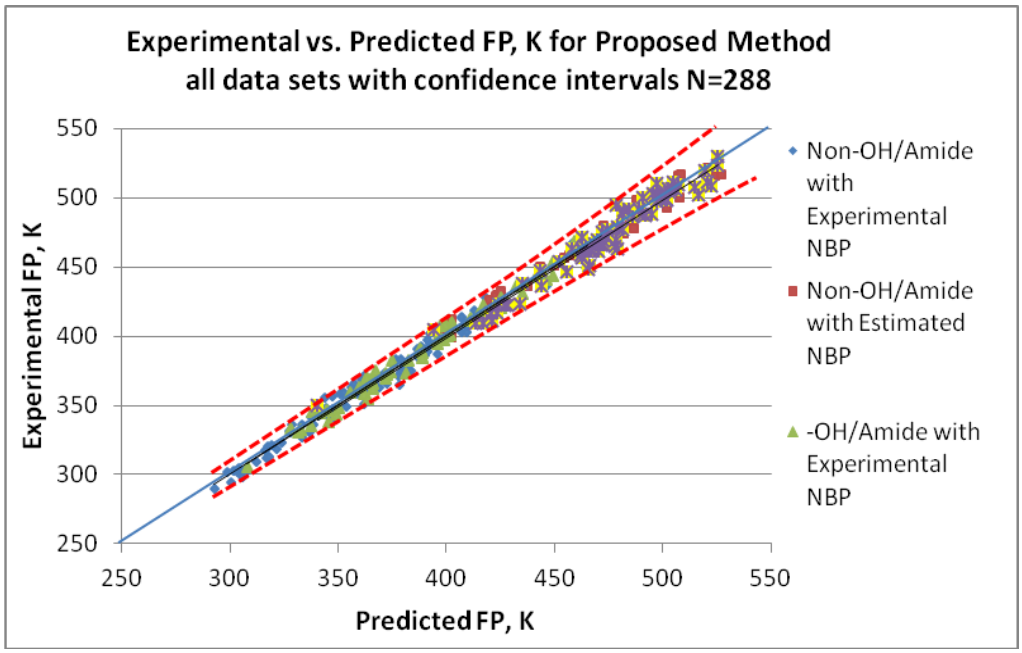

Figure 19 Experimental vs. Predicted FP for training and test datasets in Appendix A

Table 3 Molecular weight statistics of Appendix A data sets for flash point method

Mw Range (g/mol)	# of compounds
<100	8
100-150	79
150-200	46
200-250	38
250-450	48
>450	69
Total	288

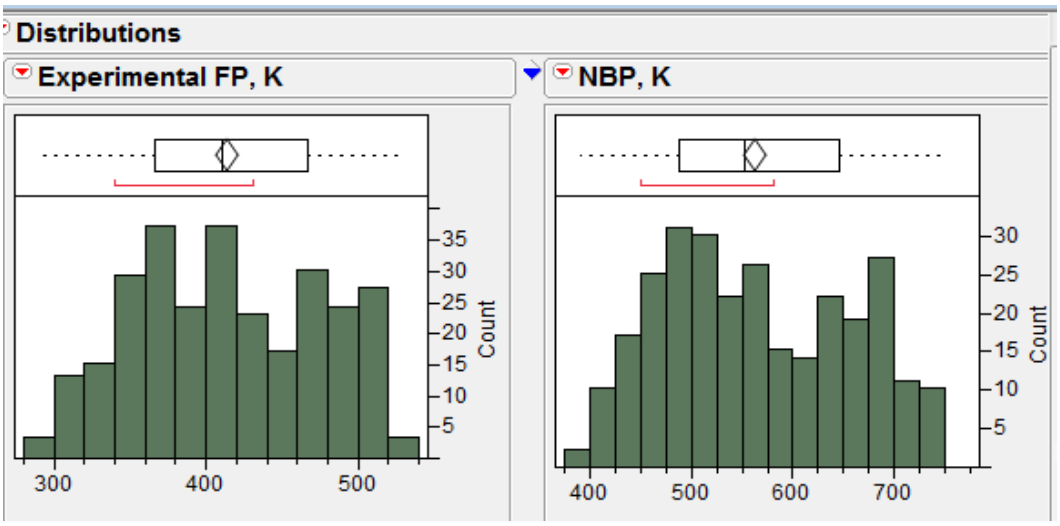

Figure 20 NBP and FP Statistics on full data set for flash point method development

Figure 21 displays the absolute deviations of the predicted minus the actual values for all data sets in Appendix A for increasing normal boiling points. One can observe the closeness of fit along the whole molecular weight range used in the data sets. There is little observable increase in deviations as molecular weight increases which validates the accuracy of the model for high molecular weight compounds.

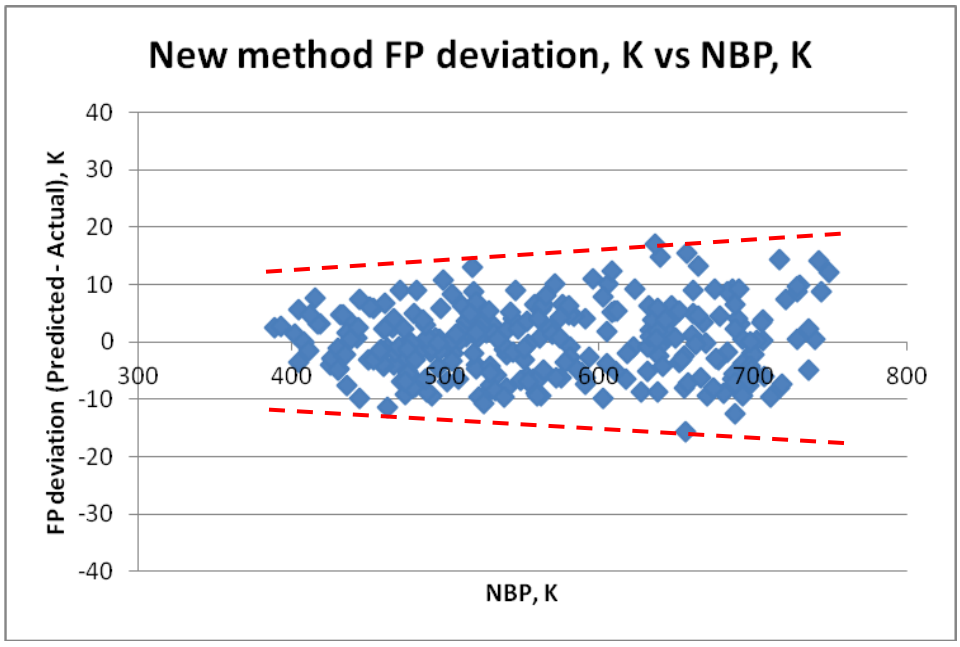

Figure 21 Proposed FP prediction method with 95% confidence intervals and behavior against all data sets in Appendix A

In Tables 4, 6 and 6 it is important to note the methods based on structure, which is a group contribution methodology based on the weights of atoms or groups in the molecule, perform the poorest for the class and types of chemicals used in these data sets. Many theories may explain why the models perform in this manner but the most likely based on studying regression models seems to point toward the fact that the experimental dataset for the models did not cover the types of high molecular weight compounds used in the datasets in this study and extrapolation is needed. Models for predicting the flash point are difficult to theoretically derive because of the complexity of the combustion thermodynamics and therefore have to rely mainly on empirical data. In this study the data set contains 117 of the 288 compounds have a molecular weight greater than 250 g/mol, ranging up to 4,000 g/mol. Therefore the proposed model is better equipped to handle this class of chemicals.

Table 4 Method comparisons by FP deviations of Appendix A training datasets, N=191

Method	Avg. Absolute Dev. K	# Chemicals >15K	Input Needed
Proposed method	3.97	0	Tb, β, Mw
Wang-Sun	7.23	17	Tb
Ishuichi	8.40	26	Tb, β
Shier	8.49	28	Tb
Catoire&Naudet	10.84	48	Tb, #C's
Patil	11.60	67	Tb
Prugh	14.26	69	Tb, β
Bodhurtha	14.07	77	Tb
Korol'chenko	22.50	98	Tb, structure
Oehley	38.12	84	Tb, structure

Table 5 Method comparisons by FP deviations of Appendix A test data sets, N=97

Method	Avg. Absolute Dev. K	# Chemicals >15K	Input Needed
Proposed method	7.27	7	Tb, β, Mw
Wang-Sun	9.53	23	Tb
Isuichi	9.63	17	Tb, β
Hshieh	11.89	29	Tb
Catoire&Naudet	11.73	21	Tb, #C's
Prugh	14.59	35	Tb, β
Bodhurtha	16.40	45	Tb
Patil	17.88	37	Tb
Korol'chenko	22.05	51	Tb, structure
Oehley	43.11	46	Tb, structure

Table 6 Method comparisons by FP deviations of both test and training datasets in Appendix A, N=288

Method	Avg. Absolute Dev. K	# Chemicals >15K	Max Deviation	Input Needed
Proposed method	5.08	7	17.46	Tb, β, Mw
Wang-Sun	8.00	40	29.21	Tb
Isuichi	8.81	43	27.96	Tb, β
Hshieh	9.63	57	32.66	Tb
Catoire&Naudet	11.14	69	50.19	Tb, #C's
Patil	13.72	104	102.91	Tb
Prugh	14.37	104	65.75	Tb, β
Bodhurtha	14.86	122	42.47	Tb
Korol'chenko	22.35	149	101.92	Tb, structure
Oehley	39.80	130	373.35	Tb, structure

THE NORMAL BOILING POINT

Introduction and Literature Review

NBP is an essential and useful physical property of a compound. There are many correlations, equations and processes that use a normal boiling point of the compound to predict another property. For many compounds this property is easily obtained through experimental procedures or accurate prediction correlations. Unfortunately for many of the high molecular weight chemicals in this study, an experimental normal boiling point is not feasible due to high temperature constraints on equipment and product decomposition at elevated temperatures or product contamination. For the compounds used in this study an accurate and reliable normal boiling point prediction correlation is needed. Normal boiling point estimation is not a new subject as shown in the list of methods in the next section. These methods have been evaluated since 1939 with Bank's[24] and then Lydersen[25] in 1955 developed a group contribution scheme for many physical properties including NBP. Joback and Reid[26] then improved on this method in 1987. In addition to group contribution methods, others have identified so called bond contribution methods, atomic contributions, molecular descriptors or Quantitative Structure-Property Relation (QSPR) based equations[27,28]. With the advent of computers and computational power, these equations have become increasingly complex; many requiring advanced knowledge of computer programming and specialized software to even use.

The objective of the normal boiling point predictive method is not to create an all encompassing method but to be specifically tailored to the molecules of interest used in the flash point prediction method. Therefore a simple, theoretically based method capable of extrapolating to high molecular weights is needed. The initial review of existing methods showed that they are

not capable of handling compounds of higher molecular weight such as those used in the flash point model development. From Figures 22, 23 and 24, one can see that although these proven methods work well for compounds in the lower molecular weight region, they become increasingly inaccurate in the high molecular weight region. This has mainly to do with the data set on which they are empirically based.

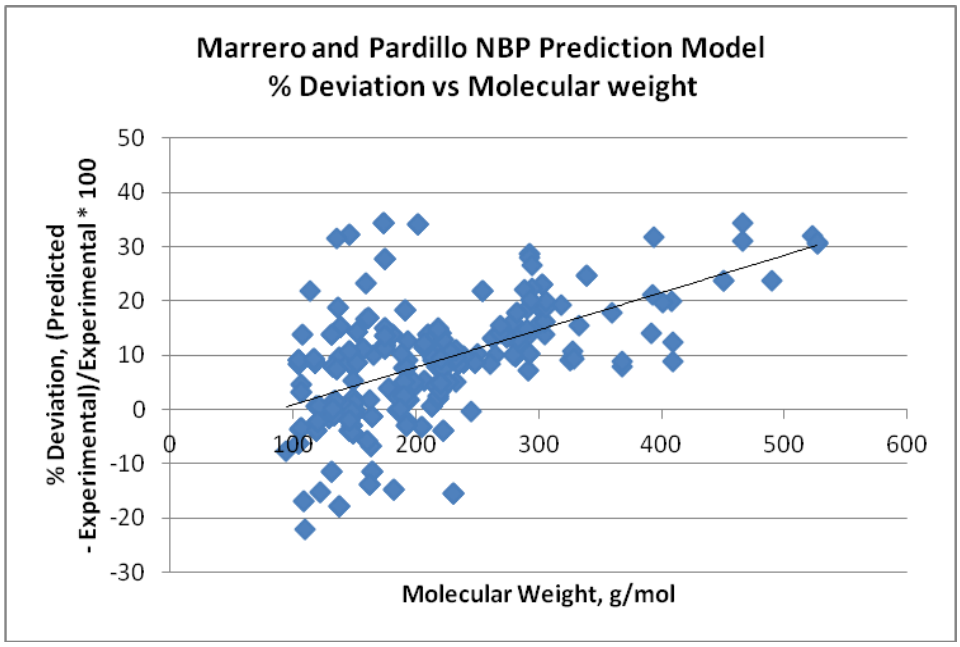

Figure 22 *Marrero and Pardillo* NBP prediction method behavior for Appendix B data set

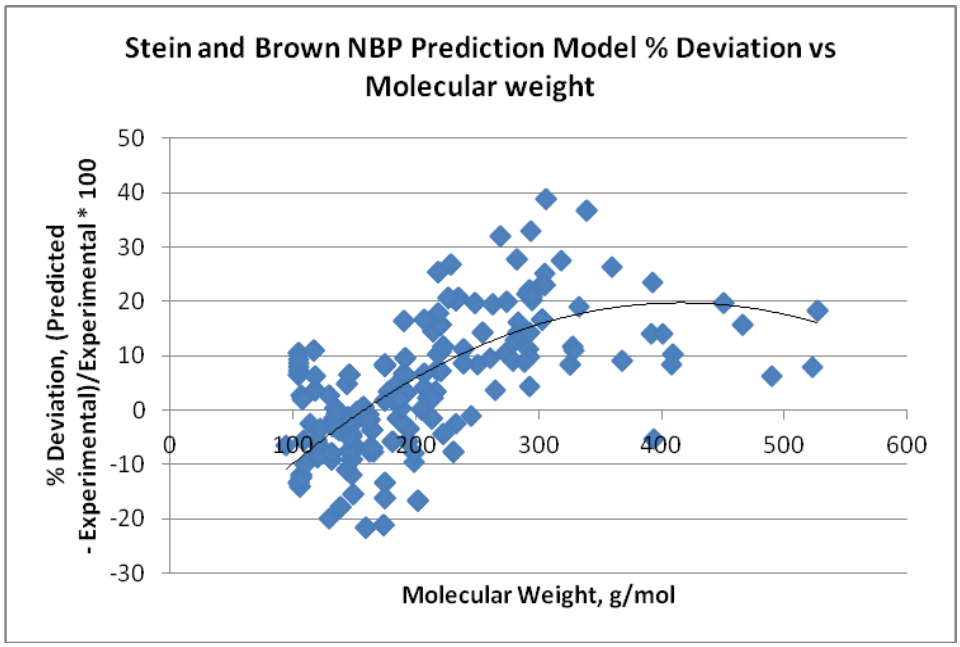

Figure 23 *Stein and Brown* NBP prediction method behavior for Appendix B data set

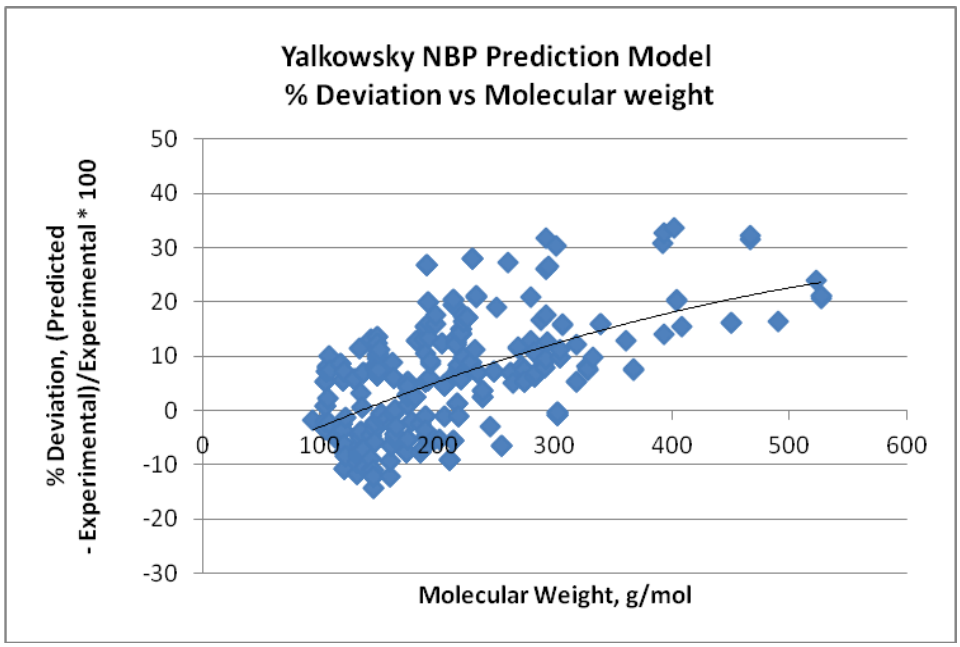

Figure 24 *Yalkowsky* NBP prediction method behaviors for Appendix B data set

One can note the particular trends of the percent deviation as a function of molecular weight. The Marrero and Pardillo[29] percent deviation trend follows a straight line showing that there is a systematic deviation of particular additive parameters of the model. The Stein-Brown[30] prediction model follows a more non-linear trend probably due to the quadratic dependence on the Joback[26] NBP. The Yalkowsky[31] Method shows a better fit for lower molecular weight compounds and shows promising extrapolation capabilities with increasing molecular weight. The Yalkowsky method seems to be the most theoretically based and possibly a reason that it captures the behavior better. Even so these methods show poor extrapolation capabilities and therefore a new method is proposed for this class of chemicals. A compilation of existing methods reviewed in this work are shown in the next section.

List of Existing Normal Boiling Point Estimation Methods

Banks[24] in 1939 devised a simple correlation of normal boiling point to molecular weight which can be applied to all chemicals. They found an absolute deviation of 8.8% of a 70 compound test set consisting of diverse functional groups and 14 poly-functional compounds[24].

$$log(T_{NBP}) = 2.98 - \frac{4}{\sqrt{M_w}} \tag{23}$$

T_{NBP} = boiling point (K)

M_w = molecular weight (g/mol)

Burnop's rule (Gold and Ogle[24]) correlates normal boiling point with molecular weight and an empirical structure factor. They found an average error of -1.46% for a test set of 255 compounds including many polar and hydrogen bonding chemicals[24].

$$log(T_{NBP}) = \frac{\sum n_i g_i}{M_w} - \frac{\mathbf{8}}{\sqrt{M_w}} \tag{24}$$

T_{NBP} = boiling point (K)

M_w = molecular weight (g/mol)

Joback and Reid (1984;1987)[26,29] re-evaluated Lydersen's[25] group contribution scheme, added several new functional groups and determined new contribution values for many physical property constants including normal boiling point, melting point and critical properties.

$$T_{NBP} = 198 + \sum_{i=1}^{k} n_i g_i \tag{25}$$

Constantinou and Gani (1994, 1995)[29,32] developed an advanced group contribution method based on the UNIFAC[34] groups but enhanced by allowing for more sophisticated functions of the desired properties and by providing contributions at a ''Second Order''.

$$T_{NBP} = 204.359 * ln\left[\sum_{i=1}^{k} n_i g_i + W * \sum_{j=1}^{m} b_j \boldsymbol{h}_j\right] \tag{26}$$

Stein and Brown (1994)[29,30] method is one of the most robust methods that can be applied to a variety chemicals with relative ease of calculation. It is an extension of the Joback method. The extension mainly covers 85 structural groups as compared to the original 45 from the Joback and Reid method. It also fits a polynomial curve to the error produced by the group contribution equation and then corrects to the fitted equation. For a 4426 compound training set, an average absolute error of 15.5K (3.2%)[24]. They evaluated their method with their own test set of 6584 chemicals and found the predicted boiling point had an absolute average deviation of 20.4K (4.3%)[24].

$$T_{NBP-SB} = -94.84 + 1.5577 * T_{NBP-JR} - 0.0007705 * T_{NBP-JR}^{2} \quad (27)$$

$$for\ T_{NBP-JR} \leq 700K$$

and

$$T_{NBP-SB} = 282.7 + 0.4791 * T_{NBP-JR} \quad (28)$$

$$for\ T_{NBP-JR} > 700\ K$$

Marrero and Pardillo (1999)[29] call their normal boiling point prediction method a group interaction contribution technique; it can also be considered as a method of *bond contributions*. They tabulate contributions from 167 pairs of atoms, such as $–CH_2–$ & –NH–, or with hydrogen attached, such as $CH_3–$ & $–NH_2$. For T_b their basic equation is;

$$T_{NBP} = \frac{\sum_{i=1}^{k} n_i b_i}{M_w^{0.4044}} + 156 \quad (29)$$

Yalkowsky and Sanghvi (2006)[33] developed a semi-empirical model for the estimation of the normal boiling points of organic compounds. The normal boiling point is calculated as the ratio of the enthalpy of boiling to the entropy of boiling. Both these values are estimated independently using a combination of additive group contribution and non-additive molecular descriptors. The main properties of the latter are the flexibility number, τ and the hydrogen bonding parameter, HBP,

$$T_{NBP} = \frac{\sum n_i g_i}{86 + 0.4 * \tau + 15 * HBP} \tag{30}$$

where,

$$\tau = (SP3 + 0.5 * SP2 + 0.5 * ring - 1)$$

$$HBP = \sqrt{(\#OH) + (\#COOH) + 0.0625(\#NH)}$$

Wilfried Cordes and Jürgen Rarey (2002)[34] developed a group contribution method for the estimation of the normal boiling point of non-electrolyte organic compounds was developed using experimental data for approximately 2500 compounds stored in the Dortmund Data Bank (DDB).

$$T_{NBP} = \frac{\sum N_i C_i}{n^a + b} + c \tag{31}$$

where a, b and c are the adjustable parameters with values of 0.6713, 1.4442 and 59.344 respectively, N_i the number of groups of type 'I', C_i the group contribution of group 'I', and n is the number of atoms in the molecule (except hydrogen).

Quantitative structure-property relationships (QSPR) are usually obtained from on-line computation from quantum mechanical methods. Thus, in most of these methods, there is no tabulation of descriptor values. Katritzky, et al. (1998) summarizes the literature for such methods applied to T_{NBP}. Egolf, et al. (1994), Turner, et al. (1998), and St. Cholokov, *et al.* (1999) also give useful descriptions of the procedures involved[29].

Normal Boiling Point Prediction Method Development

In this section the origins of the normal boiling point prediction methods are investigated to understand the prediction models and their capabilities. This is essential for creation of a new NBP prediction model. The boiling point of a substance is the temperature at which the vapor pressure of the liquid equals the environmental pressure surrounding the liquid. The normal boiling point of a liquid is the special case in which the vapor pressure of the liquid equals the defined atmospheric pressure at sea level or 1 atmosphere. Since boiling is physically a phase transition at constant temperature and pressure, it can be represented by the Gibbs free energy equation,

$$G(P,T) = H(P,T) - T \cdot S(P,T) \tag{32}$$

And for a phase transition the chemical potentials of the two phases are equal and the change in free energy between the two phases is zero. Thus;

$$G^V(P,T) - G^L(P,T) = \left(H^V - H^L\right) - T \cdot \left(S^V - S^L\right) \tag{33}$$

Therefore, at the boiling point,

$$0 = \Delta H_{vap} - T \cdot (S^V - S^L) \tag{34}$$

$$T_{NBP} = \frac{\Delta H_{vap}(T_{NBP})}{\Delta S_{vap}(T_{NBP})} \tag{35}$$

The above equation entirely describes the temperature at the boiling point if the enthalpy and entropy of boiling were able to be experimentally or theoretically observed. Unfortunately there is no simple way to measure entropy changes and therefore it must be estimated based on theory. The following shows the entropy calculation according to Ritesh Sanghvi and Samuel H. Yalkowsky[31] beginning with the statistical thermodynamic definition of entropy,

$$\Delta S_{vap}(T_{NBP}) = R ln\left(\frac{\Omega^V}{\Omega^L}\right) \tag{36}$$

where, Ω^L is the number of ways 1 mol of a material can be found that would constitute the liquid phase and Ω^V is the number of ways those molecules can exist as a gas. It is expressed more simply as a sum of translational, rotational, and conformational entropies.

$$\Delta S_{vap} = \Delta S^{Trans} + \Delta S^{Rot} + \Delta S^{Conf} \quad (37)$$

Boiling is associated with a large increase in the free volume. As a consequence, the molar volume of the compound undergoes a large increase too, and the molecules gain a large amount of translational freedom upon boiling. For most liquids, the change in the free volume upon boiling is approximately equal to the volume of its gas[19,20,31]. Since the volume of a gas is constant under normal temperature-pressure conditions, the change in the translational freedom of the molecules is nearly constant. This explains Trouton's rule of constant entropy of boiling of 88 J / (K*mol)[19,20]. The contributions of rotational and conformational freedom to the entropy of boiling are small since compounds have a large degree of rotational and conformational freedom in both the liquid and the gas phase. However, the effect of these contributions cannot be completely neglected. Trouton's rule works well for the rigid non-interacting molecules but should be modified to account for the molecular properties such as flexibility and hydrogen-bonding capability that may restrict rotational and conformational freedom in the liquid phase[19,20].

$$\Delta S_{vap} = constant + effect\ of\ flexibility + effect\ of\ hydrogen\ bonding \quad (38)$$

The flexibility parameter, τ, is calculated using the equation proposed by Dannenfelser and Yalkowsky[32], where SP3 and SP2 are the total number of non-ring, non-terminal sp3 and sp2 atoms. 'Ring' indicates the number of independent single, fused, or conjugated ring systems in the molecule. Since terminal atoms and sp hybrid atoms do not contribute to flexibility, they are not counted in the model. The rotation of hydrogen atoms is also ignored. Aliphatic cyclic groups are counted as single ring systems.

$$\tau = (SP3 + 0.5 * SP2 + 0.5 * ring - 1) \quad (39)$$

The effect of hydrogen bonding was considered as a function of the number of different hydrogen-bonding groups [–OH (alcohol), –COOH (acid group), and –NH (including –NH and –NH_2 amino groups)] present in the molecule. The hydrogen bonding parameter (HBP) is calculated using the equation proposed by Sanghvi and Yalkowsky[33] where, '#' is the number of respective groups (aliphatic or aromatic).

$$HBP = \sqrt{(\#OH) + (\#COOH) + 0.0625(\#NH)} \quad (40)$$

The molar enthalpy of vaporization at the boiling point depends on the amount of energy required to vaporize 1 mol of the liquid at its normal boiling temperature. The functional groups constituting the molecule determine the strength of the intermolecular interactions in the liquid state. The enthalpy of boiling is a function of the strength of these interactions and is related to the number and the type of groups comprising the molecule. Yalkowsky[31] assumes equation below to estimate ΔH_{vap} using a group contribution approach,

$$\Delta H_{vap} = \sum n_i g_i \quad (41)$$

where, n_i is the number of times a group appears in the compound and g_i is its contribution to the enthalpy of boiling. This method of estimating vaporization enthalpy has been used by several researchers in the past[34,35,36]. Guthrie and Taylor[34] proposed an equation both using bond and

group parameters which yielded very accurate results. For the group level parameters, 7 compounds out of 388 showed deviations of more than 1 kcal/mol, the largest being 1.6 kcal / mol[34]. Basing it solely on group contribution values does not fully capture the behavior of boiling points throughout the full molecular weight range as shown in the Stein-Brown[30] correction of the initial Joback[25] equation. Reviewing previous methods of normal boiling point estimation revealed that many used molecular weight in their model. To investigate further, studies were performed on similar families of chemicals to see if molecular weight had a strong correlation to normal boiling point. Indeed it has a strong non-linear correlation. Using these findings and the past normal boiling point estimation methods seen in section 'Review of Normal Boiling Point Estimation Methods' it was decided to include molecular weight along with the contributions of various functional groups to estimate normal boiling point. To understand the theoretical significance of molecular weight one can look to the entropy of boiling difference between the liquid and gas phases as defined by Sanghvi and Yalkowsky[31,38]. Through their analysis they have found that the entropy of boiling can be related to the Trouton constant as well as the molecular structure of the chemical as it relates to the degrees of freedom it has in the liquid phase. Flexibility and hydrogen bonding play a role when more complex and larger molecules are used. The following equation shows the relationship they play in predicting normal boiling point.

$$\Delta S_{NBP} = 87 + 0.35(\tau) + 15(HBP) \tag{42}$$

Then substituting equation (39) and (40) into (42) one gets:

$$\Delta S_{NBP} = 87 + 0.35(SP3) + 0.5SP2 + 0.5ring - 1) +$$

$$15([(\#OH) + (\#COOH) + 0.0625(\#NH)])^{0.5} \tag{43}$$

Now since the molecules of interest in our study have mainly SP3 hybridized carbons and on average have at least one alcohol group as well as one primary or secondary amine group we can simplify their equation to the one below,

$$\Delta S_{NBP} = 87 + 0.35(SP3) + 15(1)^{0.5} \tag{44}$$

Simplifying one arrives at:

$$\Delta S_{NBP} \sim M_W^n \tag{45}$$

So inserting equations (41) and (45) into equation (35), for theoretical normal boiling, one arrives at the proposed NBP prediction model,

$$T_{NBP} = \frac{A + \sum_{i=1}^{n} g_i n_i}{M_W^n} \tag{46}$$

where, T_{NBP} is the normal boiling point temperature (^{o}C) and M_W is the molecular weight of the compound in grams per mol. Equation (46) is similar to the one used in the Marrero and Pardillo[34] and Cordes and Rarey[32] group bonding method. The next step was to determine which functional groups were to be used in the model.

Previous models were examined to understand the functional groups and combination of atoms or molecules that represented the best correlation to normal boiling point. This was done by analyzing the numerical contributions of groups in other models as well as understanding the distribution of groups in the dataset. Since the –OH group can be attached to different carbon atoms one may think to use all possible alcohol groups in the model but that would require many more parameters and a much bigger dataset. Analysis shows that only small differences in value between alcohol groups on different carbons were found. It was also noted that because of the types of molecules used such as long chain alkoxylated alcohols and amines it was decided to tune the model parameters to be specific to Huntsman specialty products for increased accuracy. Therefore the alkoxylated groups are used as model parameters. Table 7 shows the functional group name and characteristics of its chemical structure. From the table one can note that the groups are independent of the bond type. The oxygen (O) group was introduced to account for any molecule that does not have alkoxylated groups present. In appendix B training data set some molecules are duplicated to account for both oxygen (O) groups and alkoxylated groups if they displayed characteristics of both. Usually these are smaller molecules with no more than one or two oxygen groups.

Table 7 Parameters used in normal boiling point group contribution model

Parameter Name	**Chemical Structure**
Normal Carbon (**C**),	-CH3, -CH2-, >CH-, >C<
Alcohol (**OH**),	-OH (any bond)
Ethylene Oxide (**EO**),	-(O-CH2-CH2)-
Propylene Oxide (**PO**),	-(O-CH2-CH(CH3))-
Butylene Oxide (**BO**),	-(O-CH2-CH(CH2-CH3))-

Oxygen (**O**),	-O- (other than EO, PO, BO)
Primary Amine (**NH2**),	-NH2 (any bond)
Sec. Amine (**NH**),	-NH- (any bond)
Tertiary Amine (**N**),	>N- (any bond)
Benzene Ring (**B**)	($C_6H_{6-\#bonds}$) (any bond)

Figure 25 shows two examples of how the groups are identified within a compound. In these compounds one can use either the (EO) group or oxygen (O) group since no repeating chains are present.

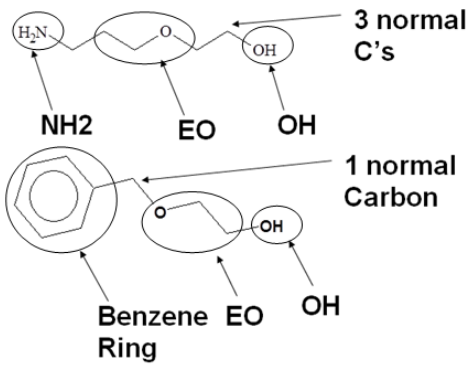

Figure 25 Visual depictions of groups used in normal boiling point group contribution model

The model parameters consisting of the groups are regressed via JMP®8.0.2 statistical analysis software at different values of exponent 'n' on molecular weight. This was done because the software cannot handle non-linear equations of this kind. The optimal value of 'n' with the model parameters was 0.9. The data set comes from the DIPPR® 801 database and Huntsman data base. To be able to have a model capable of extrapolation to higher molecular weights it is apparent that the training set contains compounds with high molecular weight, more so than previous models. This was accomplished by introducing compounds that had an extrapolated NBP based on lower vapor pressure data.

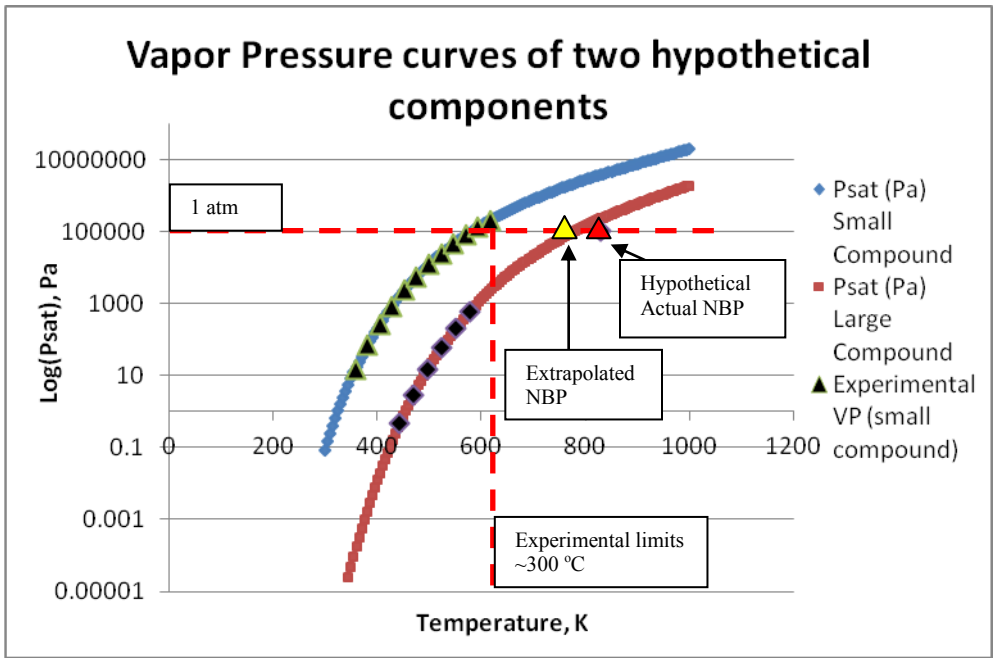

Figure 26 Method of retrieving high molecular weight normal boiling points using vapor pressure correlations

From Figure 26 one can observe the large and small compound vapor pressure curves. The small compound has experimental data up to atmospheric pressure while the large does not due to experimental limitations. The large compound will either decompose at higher temperatures or experimental capabilities cannot handle these high temperatures. Therefore an extrapolated NBP, from experimental low vapor pressure data and vapor pressure correlation, was retrieved. Since extrapolations are not experimental values and are subject to more error, weight values are assigned to each compound in the regression of the model so large errors will not influence the regression. The weights are based on the ratio of highest experimentally measured vapor pressure data point over atmospheric pressure with 1 being the highest value and 0 being the lowest. If the chemical has a ratio between 0.75-1 then it is weighted four times in the

regression. Similarly if the chemical has a ratio of 0.5-0.75 it is weighted 3 times, 0.25-0.5 it is weighted 2 times and 0-0.25 it is weighted once. Figure 27 shows the multivariate linear regression of the training dataset in appendix B. The high R-square value shows the strength of the fit.

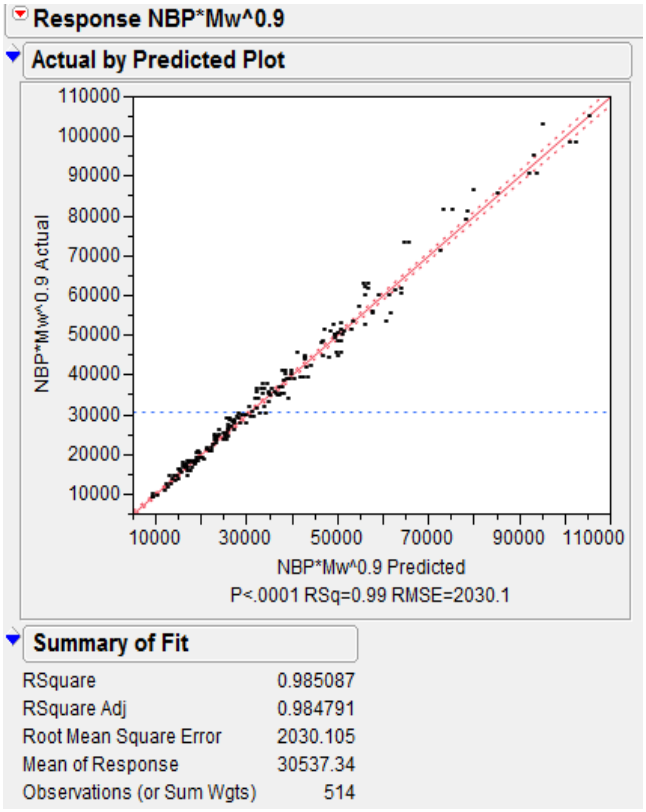

Figure 27 Regression analysis of normal boiling point prediction method

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	10	1.3636e+11	1.364e+10	3365.178
Error	502	2034120358	4052032.6	Prob > F
C. Total	512	1.3839e+11		0.0000*

Lack Of Fit

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|	VIF
Intercept	-17286.02	328.1714	-52.67	<.0001*	.
C	3025.954	27.73881	109.09	0.0000*	1.2701915
OH	7857.365	127.1166	61.81	<.0001*	1.3834261
EO	9745.4079	81.28622	119.89	0.0000*	1.3704609
PO	11787.532	102.358	115.16	0.0000*	1.2235913
BO	14419.465	312.5859	46.13	<.0001*	1.0988994
O	4407.5311	196.4832	22.43	<.0001*	1.117928
NH2	7186.5074	158.9386	45.22	<.0001*	1.3711025
NH	5287.0972	178.5616	29.61	<.0001*	1.232886
N	3764.581	158.6599	23.73	<.0001*	1.3353694
Benzene	21413.697	212.1895	100.92	0.0000*	1.5220878

Figure 28 Statistical analysis of proposed model parameters

The parameter values for the model are shown in Figure 28 above. They are used in equation (40). The t-ratio describes the correlation strength of the parameter as defined in section 'Flash Point Method Development'. The 'VIF' column shows the degree of variance inflation the parameter displays due to correlation between parameters. Here one can observe there is no inter-dependence of any of the variables. They From statistics, a variance inflation factor of 1 implies no co-linearity between parameters while a 'VIF' of 10, implies serious co-linearity problems.. One can observe the (EO) parameter has the highest correlation strength, t-ratio, and the (O) parameter has the lowest. Even so all the parameters are highly correlative given the low p-value for the significance test.

Figure 29 displays the statistical fit of the predicted NBP values from the proposed method to the experimental values used. The dashed red lines show the 95% confidence interval for an

individual predicted value. One can have 95% confidence that a NBP value will be with ± 30 C using this prediction model.

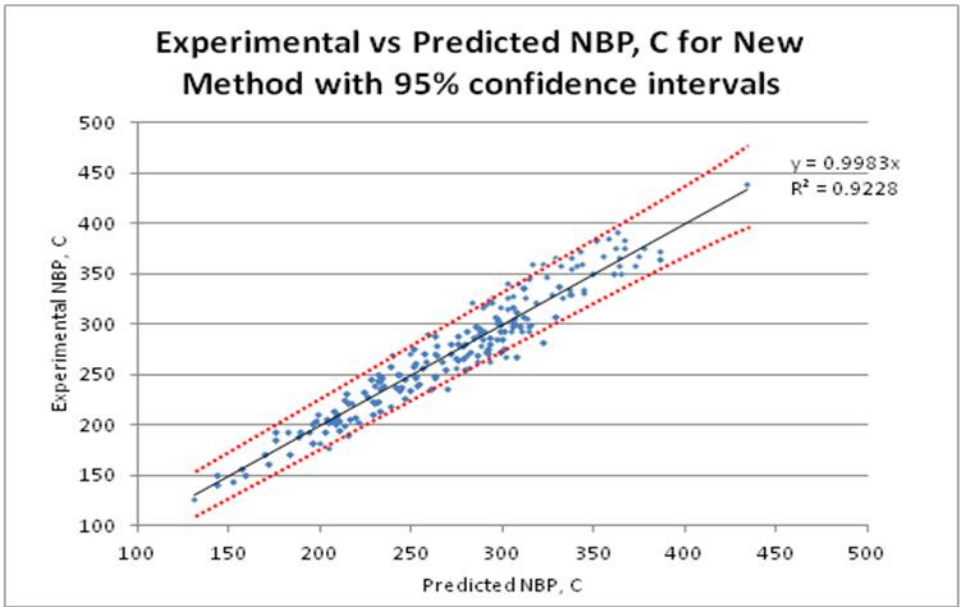

Figure 29 Fit of Experimental vs. Predicted NBP using proposed NBP prediction model

Normal Boiling Point Method Analysis and Comparisons

Shown below, figures 30 and 32 shows the residual plot of the deviations of the experimental data from the predicted NBP for each entry. One can observe that the model fits the data quite well and the residuals are distributed normally about zero implying no abnormalities in the model. Figure 31 displays the percent deviation as the molecular weight increases and shows no trend of increasing deviations which supports extrapolative capabilities.

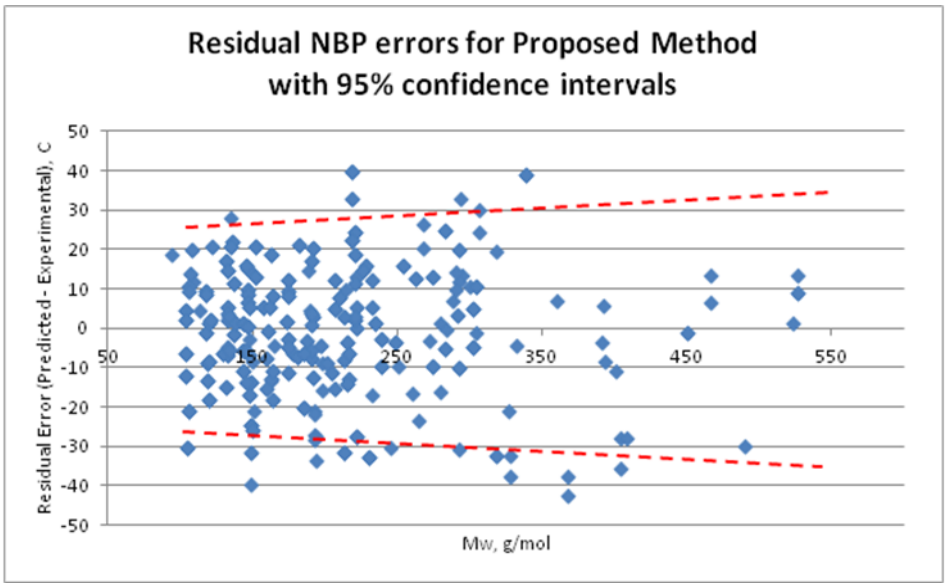

Figure 30 Residual deviations versus the molecular weight for the proposed NBP method

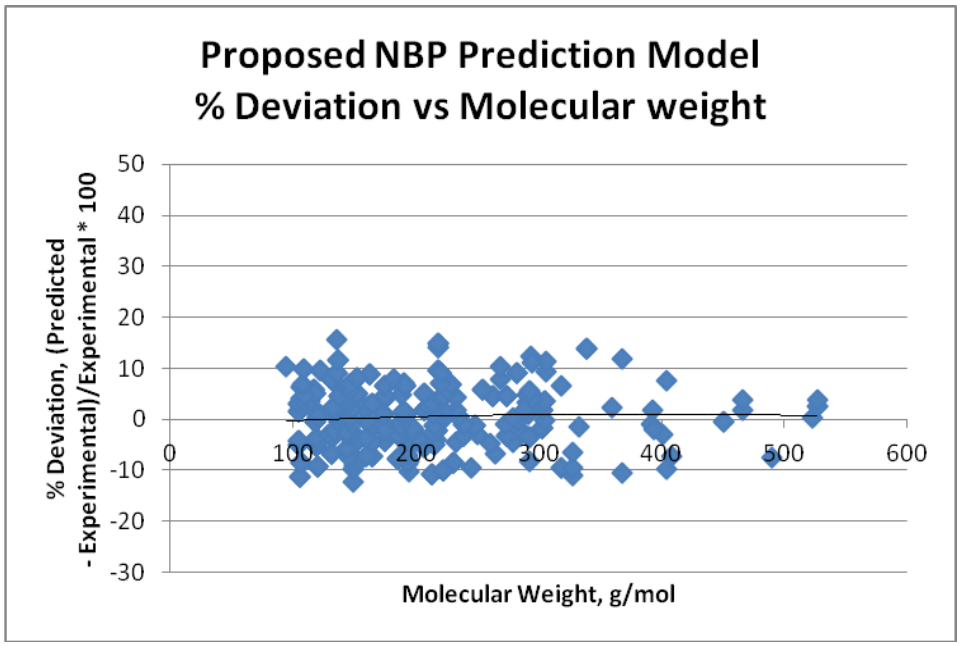

Figure 31 Percent deviations versus the molecular weight for the proposed NBP method

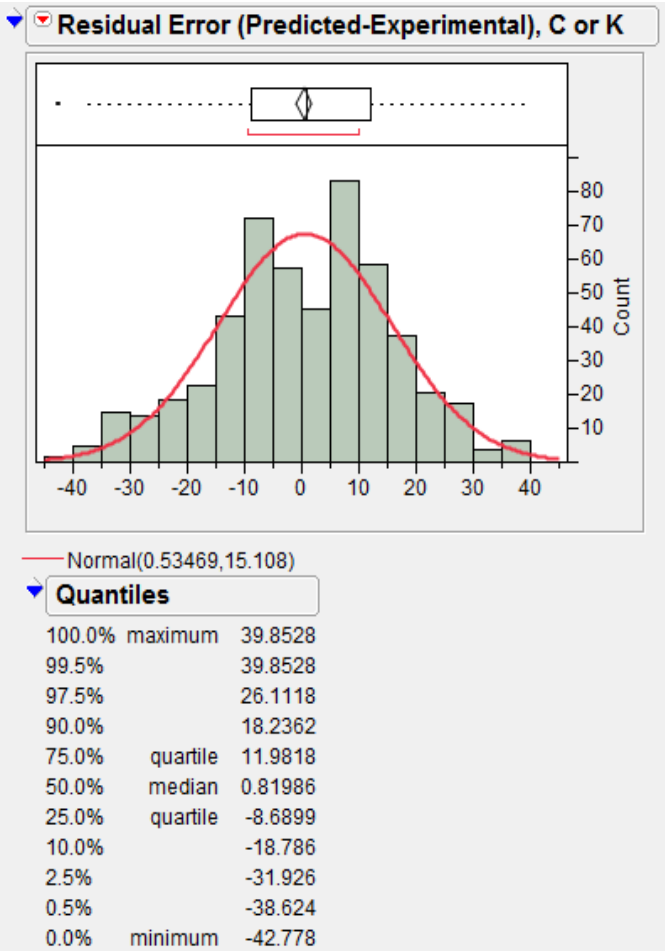

Figure 32 Residual NBP values histogram using proposed method

In order to validate making a new model it is important to understand the behavior of past models. Table 8 shows the performance statistics of the various models tested using the data set in appendix B. The percent deviation is the residual value, predicted minus actual NBP, divided by the actual NBP in ^{o}C multiplied by 100.

Table 8 Statistical comparisons of other methods to the proposed model

Method	**AAD, ^{o}C**	**AA%D**	**>10% error**	**>40 ^{o}C deviation**
Stein-Brown Method[33]	25.60	9.69	76	46
Yalkowsky[22]	23.42	8.46	68	28
Marrero-Pardillo[34]	19.73	7.32	71	37
*Nannoolal[38]	19.50	7.24	14	8
Our Method	12.24	4.85	10	3

*Fit to only 122 of the 196 chemicals in Appendix B data set

It is important to test how a method works outside the regression data set and whether it captures behaviour of certiain classes of chemicals. In Figures 33 and 34 one can observe the trend of slightly branched and linear alkanes, alcohols and amines. The method seems to capture the trend of each chemical class with increasing weight showing that the groups used are accurately weighted in the model. The point of this analysis is to show the model behaviour and not prove superior accuracy for these chemicals. These family of chemicals are simple linear chains and not the more exotic poly-functional compounds that the proposed model intends to predict.

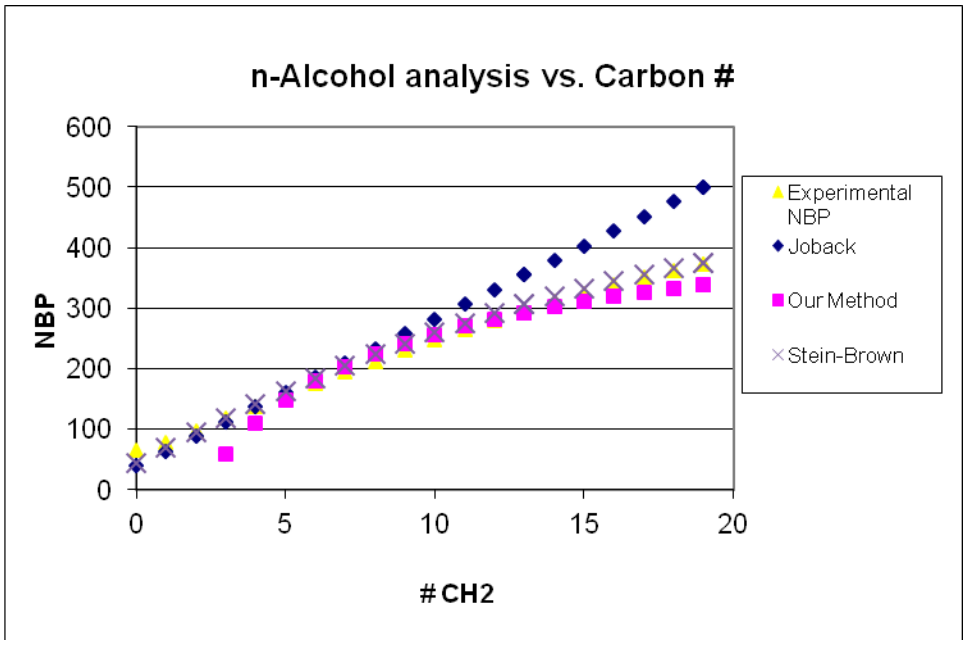

Figure 33 Comparative analysis of new NBP prediction method for family of n-alcohols

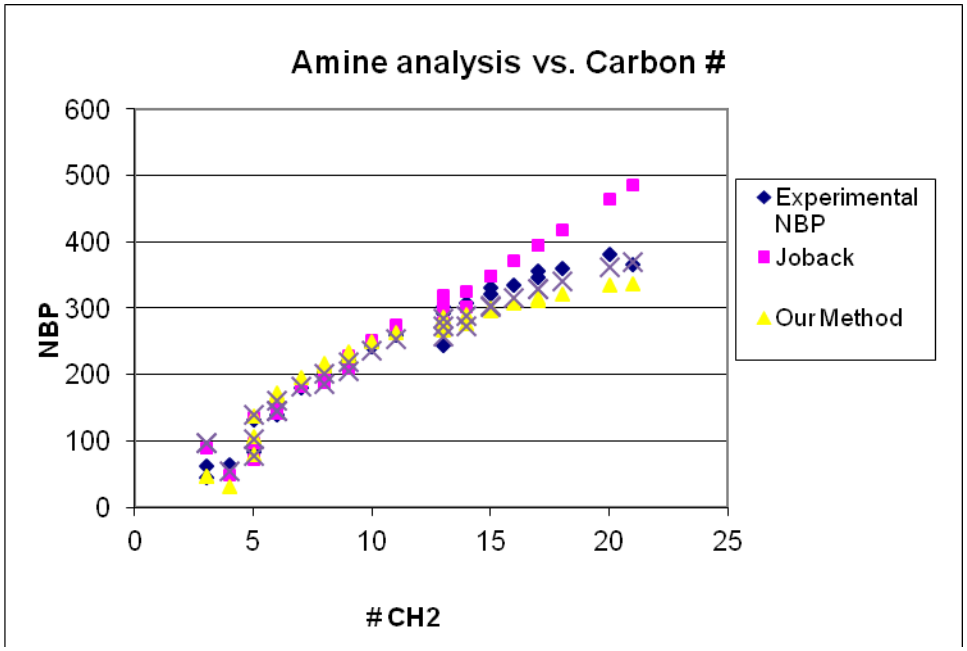

Figure 34 Comparative analysis of new NBP prediction method for family of n-amines

SUMMARY AND CONCLUSIONS

Summary

This report has covered the critical review and estimation of flash points of high molecular weight poly-functional C, H, N, O compounds by creating a new model which captures the behavior of this new chemical class. The method proposed is based on the normal boiling point of the compound and its chemical structure. To be able to critically review these compounds it was found that a new normal boiling point prediction method was needed for the selected chemical class because experimental techniques and past estimation methods cannot be used on these compounds. Critical data analysis was also performed on the training and test data sets to increase accuracy of the flash point prediction method proposed. This analysis also allowed for retesting of the flash points of compounds that were found suspect, according to the analysis in this work, at the Huntsman advanced technology center. It found that data for many of the reported flash point values for the compounds were indeed erroneous. The normal boiling point prediction model was used to establish normal boiling point temperature values of high molecular weight compounds for use in the prediction of their flash points. Given the good fit of the model with the data it is evident that the NBP prediction model is valid. The normal boiling point model gives a fit of absolute average deviation of 12K and maximum deviation of 40K for a diverse set of 196 compounds with molecular weights up to 600 g/mol. The fit gives an overall deviation of 5 ^{o}C and max deviation of 17.5 ^{o}C for total data set of 288 diverse chemicals of molecular weights up to 4,000 g/mol.

Conclusions

In this work there are three key findings:

1. The flash point model accurately correlates the physical behavior of this class of chemicals up to 4000 molecular weight. It predicts the flash points of the high molecular weight poly-functional C, H, N, O compounds. The data analysis and other findings show that there is no substantial decomposition behavior of these high molecular weight chemicals at the flash point temperature.
2. The normal boiling point prediction model is based on high molecular weight poly-functional C, H, N, O compounds specifically targeted to the specialty chemical compounds used in the flash point analysis. This includes molecular weights up to 600 g/mol and is used to extrapolate the NBP of this class of chemicals up to 4000 molecular weight.
3. The review of existing MSDS and data base flash point values uncovered suspect data points that were tested in a Penksy-Martens closed cup flash point tester in a Huntsman facility. New flash point data values for those compounds are reported in this work. They appear to have been correctly identified as erroneous by the analysis in this work.

Future Work

Future work in this area should involve the additional review and prediction of flash points of high molecular weight compounds including those containing sulfur, halogen, phosphorus atoms and more exotic functional groups such as cyano, imid, imines and nitro. Even though three phosphorus based compounds were analyzed in the test data set, the behavior at higher molecular weights was not validated due to availability of accurate data. Other methods claim to be able to predict organo-phosphorus compounds but these are only low molecular weight compounds[10].

New studies on phosphorus based flame retardants also warrant more analysis and research into the flash point behavior of high molecular weight organo-phosphorus compounds[39]. The review and update of physical properties for these chemicals is also essential for safe operations. Future work should be done to characterize important physical properties for these types of chemicals. For instance, using the flash point model and the normal boiling point model it is possible to get more physical property data seeing that these two points can represent two vapor pressure points. Another vapor pressure point could be derived from the method proposed by Jef Rowley[2]. Coupled with low pressure data one may obtain a full vapor pressure curve up to the NBP. The enthalpy of vaporization can then be estimated with sufficient accuracy using the vapor pressure curve.

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APPENDIX A

Table A1 Training data set for flash point method; non-alcohol and non-amide containing compounds

Chemical Name	CAS	Reference	Chemical Formula	Mw	NBP, C	FP, C
N,N-dimethyl formamide	68-12-2	Dippr® 801 Database	C3H7NO	73.0	152.0	58.0
4-methylpyridine	108-89-4	Dippr® 801 Database	C6H7N	93.0	145.0	36.0
1-methyl-2-pyrrolidinone	872-50-4	Dippr® 801 Database	C5H9NO	99.0	202.2	90.0
2-ethyloxazoline	10431-98-8	Sigma Aldrich MSDS	C5H9NO	101.0	128.4	29.0
Hexylamine	111-26-2	Dippr® 801 Database	C6H15N	101.0	131.0	29.0
N-methylmorpholine	109-02-4	Huntsman MSDS	C5H9NO	101.2	115.6	17.0
N,N-DIMETHYL-1,3-PROPANEDIAMINE	109-55-7	Dippr® 801 Database	C5H14N2	102.0	134.5	30.9
Dimethylaminopropylamine	109-55-7	Huntsman MSDS	C5H14N2	102.2	134.9	31.0
1,2-dimethylbenzene	95-47-6	Sigma Aldrich MSDS	C8H10	106.0	144.0	31.0
m-PHENYLENEDIAMINE	108-45-2	Dippr® 801 Database	C6H8N2	108.0	286.9	138.0
N-ethylmorpholine	100-74-3	Dippr® 801 Database	C6H12NO	115.2	138.5	30.0
Heptylamine	111-68-2	Sigma Aldrich	C7H17O	115.2	156.9	44.0
4-FORMYLMORPHOLINE	4394-85-8	Dippr® 801 Database	C5H9NO2	115.2	240.0	113.0
PHTHALAN	496-14-0	Huntsman MSDS	C8H8O	120.0	192.0	68.9
2,3-dimethylaniline	87-59-2	Dippr® 801 Database	C8H11N	120.0	222.0	96.0
N-EthylAniline	103-69-5	Dippr® 801 Database	C8H11N	121.2	204.6	85.0
2,6-DIAMINOTOLUENE	823-40-5	Dippr® 801 Database	C7H10N2	122.0	283.9	145.9
N-ETHYLCYCLOHEXYLAMINE	5459-93-8	Sigma Aldrich MSDS	C8H17N	127.0	165.0	45.0
N,N-dimethylcyclohexylamine	98-94-2	Sigma Aldrich MSDS	C8H17N	127.0	158.5	39.0
N,N-Dimethylcyclohexylamine	98-94-2	Sigma Aldrich MSDS	C8H17N	127.2	160.0	40.0
2-ethyl-1-hexanamine	104-75-6	Sigma Aldrich MSDS	C8H19N	129.0	169.0	50.0
N-aminoethylpiperazine (AEP)	140-31-8	Dippr® 801 Database	C6H15N3	129.2	220.8	94.0
Diisobutylamine	110-96-3	Sigma Aldrich MSDS	C8H19N	130.0	138.0	30.0

Chemical Name	CAS	Reference	Chemical Formula	Mw	NBP, C	FP, C
Dibutylether	142-96-1	Sigma Aldrich MSDS	C8H18O	130.0	142.4	25.0
3-butoxypropylamine	16499-88-0	Dippr® 801 Database	C7H17NO	131.0	177.0	63.0
2-METHYLBENZOFURAN	4265-25-2	Dippr® 801 Database	C9H6O	132.2	197.0	67.0
DIETHYLENE GLYCOL DIMETHYL ETHER	111-96-6	Sigma Aldrich MSDS	C6H14O3	134.0	162.0	57.0
Benzyldimethylamine	103-83-3	Huntsman MSDS	C9H13N	135.2	180.0	54.0
p-CRESIDINE	120-71-8	Sigma Aldrich MSDS	C8H11NO	137.0	235.0	110.0
p-PHENETIDINE	156-43-4	Dippr® 801 Database	C8H11NO	137.2	253.9	115.9
Aminopropylmorpholine	123-00-2	Huntsman MSDS	C7H16N2O	144.2	224.1	90.0
Triethylenetetramine	112-24-3	Sigma Aldrich MSDS	C6H18N4	146.2	266.5	129.0
Diethylaniline	91-66-7	Dippr® 801 Database	C10H15N	149.2	216.2	85.0
1-ETHYLNAPHTHALENE	1127-76-0	Huntsman MSDS	C12H12	156.0	258.3	111.0
1-decanamine	2016-57-1	Dippr® 801 Database	C10H23N	157.3	220.5	85.0
4-(2-(diMethylAmino)Ethyl)Morpholine	4385-05-1-	Sigma Aldrich MSDS	C8H18N2O	158.2	206.0	76.0
n-BUTYL VALERATE	591-68-4	Dippr® 801 Database	C9H18O2	158.3	186.5	63.0
ETHYLENE GLYCOL MONOBUTYL ETHER ACETATE	112-07-2	Huntsman MSDS	C8H16O3	160.2	192.0	71.0
Cyclohexylbenzene	827-52-1	Dippr® 801 Database	C12H16	160.3	240.1	98.9
METHYL-4-FORMYLBENZOATE	1571-08-0	Dippr® 801 Database	C9H8O3	164.1	270.8	129.9
dipentylether	693-65-2	Sigma Aldrich MSDS	C10H22O	166.0	187.5	57.0
DIBENZOFURAN	132-64-9	Huntsman MSDS	C12H8O	168.2	285.2	130.0
DIPHENYLAMINE	122-39-4	Dippr® 801 Database	C12H11N	169.0	302.0	152.9
p-AMINODIPHENYL	92-67-1	Dippr® 801 Database	C12H11N	169.0	336.9	166.0
ISOPHORONE DIAMINE	2855-13-2	Sigma Aldrich MSDS	C10H22N2	170.0	247.0	110.0
Diphenyl ether	101-84-8	Sigma Aldrich MSDS	C12H10O	170.2	258.3	115.0
ISOPENTYL ISOVALERATE	659-70-1	Dippr® 801 Database	C10H20O2	172.3	194.0	71.9
Pentamethyldiethylenetriamine	3030-47-5	Huntsman MSDS	C9H23N3	173.3	201.0	83.3
DODECANAL	112-54-9	Dippr® 801 Database	C12H24O	184.3	248.9	101.0

Chemical Name	CAS	Reference	Chemical Formula	Mw	NBP, C	FP, C
p-Aminodiphenylamine	101-54-2	Dippr® 801 Database	C12H12N2	184.4	354.0	193.4
TriButylAmine	102-82-9	Dippr® 801 Database	C12H27N	185.4	214.0	86.1
Tetramethyldipropylenetriamine	6711-48-4	Dippr® 801 Database	C10H25N3	187.3	235.4	98.0
DIPROPYLENE GLYCOL MONOMETHYL ETHER ACETATE	88917-22-0	Dippr® 801 Database	C9H18O4	190.2	209.3	85.9
EDR-192	929-75-9	Huntsman MSDS	Proprietary	192.0	289.2	154.4
DIALLYL MALEATE	999-21-3	Dippr® 801 Database	C10H12O4	196.2	246.9	119.9
DIBENZYL ETHER	103-50-4	Huntsman MSDS	C14H14O	198.0	288.3	135.0
TRIDECANAL	10486-19-8	Dippr® 801 Database	C13H26O	198.3	267.0	115.9
2-ETHYLHEXYL ACETATE	103-09-3	Dippr® 801 Database	C10H20O2	172.3	199.8	72.0
Tetraethylenepentamine (TEPA)	112-57-2	Dippr® 801 Database	C8H23N5	200.0	333.0	162.9
Pentamethyldipropylenetriamine	3855-32-1	Huntsman MSDS	C11H27N3	201.4	227.0	92.0
DIETHYLENE GLYCOL MONOBUTYL ETHER ACETATE	124-17-4	Sigma Aldrich MSDS	C10H20O4	204.3	245.0	102.0
octyl 2-methyl butyrate	110-39-4	The Good Scent Company	C13H26O2	214.3	250.0	104.5
n-BUTYL NONANOATE	50623-57-9	Dippr® 801 Database	C13H26O2	214.0	246.5	98.0
2-ACETOACETOXY ETHYL METHACRYLATE	21282-97-3	Dippr® 801 Database	C10H14O5	214.2	274.0	133.9
DIETHYLENE GLYCOL DI-n-BUTYL ETHER	112-73-2	Huntsman MSDS	C12H26O3	218.0	256.0	118.0
TETRAETHYLENE GLYCOL DIMETHYL ETHER	143-24-8	Huntsman MSDS	C10H22O5	222.7	275.8	141.0
DIBUTYL MALEATE	105-76-0	Dippr® 801 Database	C12H20O4	220.2	280.0	139.9
p-Terphenyl	92-94-4	Dippr® 801 Database	C18H14	230.0	382.0	206.9
Poly(propylene glycol) bis(2-aminopropyl ether)	9046-10-0	Sigma Aldrich MSDS	Proprietary	230.9	260.0	124.0
DI-n-OCTYLAMINE	1120-48-5	Huntsman MSDS	C16H35N	241.5	307.7	144.7
di-n-octyl ether	629-82-3	Sasol MSDS	C16H34O	242.0	286.0	138.0
HK-511	194673-87-5	Huntsman MSDS	Proprietary	283.0	290.2	138.0
2,2,4-TRIMETHYL-1,3-PENTANEDIOL DIISOBUTYRATE	6846-50-0	Dippr® 801 Database	C16H30O4	286.4	280.0	125.9
DIBUTYL SEBACATE	109-43-3	Dippr® 801 Database	C18H34O4	314.2	349.0	178.0

Chemical Name	CAS	Reference	Chemical Formula	Mw	NBP, C	FP, C
Surfonamine B-30	No CAS#	Huntsman MSDS*	Proprietary	321.1	315.3	155.5
Tri-n-Octylamine	1116-76-3	Dippr® 801 Database	C24H51N	353.7	366.0	183.9
DIOCTYL ADIPATE	123-79-5	Dippr® 801 Database	C22H42O4	370.5	404.9	217.0
1,2-BENZENEDICARBOXYLIC ACID, HEPTYL, NONYL ESTER	19295-81-9	Dippr® 801 Database	C24H38O4	390.5	414.0	226.9
DIISOOCTYL PHTHALATE	27554-26-3	Dippr® 801 Database	C24H38O4	390.5	420.9	230.9
DIOCTYL PHTHALATE	117-81-7	Sigma Aldrich MSDS	C24H38O4	391.0	385.0	207.0
XTJ-582	9046-10-0	Huntsman MSDS*	Proprietary	398.8	358.5	185.0
JEFFAMINE D 400	9046-10-0	Huntsman MSDS*	Proprietary	427.8	332.0	163.0
TRIETHYLENE GLYCOL BIS(2-ETHYLHEXANOATE)	94-28-0	Dippr® 801 Database	C22H42O6	402.0	387.8	199.0
1,2-BENZENE DICARBOXYLIC ACID, HEPTYL, UNDECYL ESTER	65185-88-8	Dippr® 801 Database	C26H42O4	418.0	433.9	233.0
Jeffamine T 403	39423-51-3	Huntsman MSDS*	Proprietary	432.4	368.3	195.0
Trioctyl Trimellitate	3319-31-1	Dippr® 801 Database	C33H54O6	546.0	424.8	233.0
Surfonamine B-100	No CAS#	Huntsman MSDS*	Proprietary	1003.0	379.1	193.3
Surfonamine MNPA 1047	No CAS#	Huntsman MSDS*	Proprietary	1211.8	410.4	201.0
XTJ-602	No CAS#	Huntsman MSDS*	Proprietary	1457.0	414.2	216.0
Surfonamine B-200	No CAS#	Huntsman MSDS*	Proprietary	1977.0	417.4	205.0
Surfonamine L-207	83713-01-3	Huntsman MSDS*	Proprietary	2003.0	446.0	243.3
Jeffamine M 2005	83713-01-3	Huntsman MSDS*	Proprietary	2063.8	420.4	225.0
Surfonamine L-200	83713-01-3	Huntsman MSDS*	Proprietary	2067.0	457.6	235.0
XTJ-509	64852-22-8	Huntsman MSDS*	Proprietary	2989.0	438.1	235.0
Surfonamine L-300	83713-01-3	Huntsman MSDS*	Proprietary	3047.0	476.7	243.3
Surfonic C-100	No CAS#	Huntsman MSDS*	Proprietary	1630.2	418.5	209.5
Surfonamine L-300	83713-01-3	Huntsman MSDS*	Proprietary	3016.8	467.5	248.3
JEFFAMINE M 3003	83713-01-3	Huntsman MSDS*	Proprietary	2898.1	471.2	243.0

*Reference gives experimental flash point value but normal boiling point is estimated by equation (39)

Table A2 Training data set for flash point method; -OH and amide containing compounds

Chemical Name	CAS	Reference	Chemical Formula	Mw	NBP, C	FP, C
CYCLOPROPANECARBOXAMIDE	6228-73-5	Dippr® 801 Database	C4H7NO	85.0	255.0	142.0
1,3-DIMETHYL UREA	96-31-1	Sigma Aldrich MSDS	C3H8N2O	88.0	269.0	147.0
1,2-butanediol	584-03-2	Dippr® 801 Database	C4H10O2	90.0	196.4	93.4
2-PENTOXYETHANOL	6196-58-3	Dippr® 801 Database	C7H16O2	132.0	187.5	75.0
PROPYLENE GLYCOL MONOMETHYL ETHER	107-98-2	Sigma Aldrich MSDS	C4H10O2	90.0	120.1	32.0
DiEthylene-Glycol-Propyl-Ether	6881-94-3	Sigma Aldrich MSDS	C7H16O3	148.2	214.0	96.0
Tert-BUTYLFORMAMIDE	2425-74-3	Dippr® 801 Database	C5H11NO	101.2	202.0	95.0
PROPYLENE GLYCOL n-BUTYL ETHER	5131-66-8	Dippr® 801 Database	C7H16O2	132.0	170.0	62.0
n-PENTANOIC ACID	109-52-4	Dippr® 801 Database	C5H10O2	102.0	185.8	86.0
DIETHYLENE GLYCOL BUTYL ETHER	112-34-5	Sigma Aldrich MSDS	C8H18O3	162.0	231.0	109.0
DIPROPYLENE GLYCOL	25265-71-8	Huntsman MSDS	C6H14O3	134.0	231.4	117.9
1-hexanol	111-27-3	Dippr® 801 Database	C6H14O	102.2	156.8	59.9
4-methyl-1-pentanol	626-89-1	Sigma Aldrich MSDS	C6H14O	102.0	162.5	57.0
p-EthylPhenol	123-07-9	Dippr® 801 Database	C8H10O	122.2	218.0	100.0
p-Cresol	106-44-5	Dippr® 801 Database	C7H8O	108.1	202.0	94.9
2-methylcyclohexanol	7443-70-1	Dippr® 801 Database	C7H14O	114.0	165.0	59.0
3-ETHYL-1-HEPTANOL	3525-25-5	Dippr® 801 Database	C9H20O	144.3	207.0	89.9
HEXANAMIDE	628-02-4	Dippr® 801 Database	C6H13NO	115.2	256.0	136.9
6-AMINOHEXANOL	4048-33-3	Dippr® 801 Database	C6H15NO	117.2	223.0	116.8
Methyldiethanolamine	105-59-9	Dippr® 801 Database	C5H13NO2	119.0	247.6	126.9
n-(2-HYDROXYETHYL)PIPERAZINE	103-76-4	Dippr® 801 Database	C6H14N2O	130.2	245.4	124.0
2-octanol	123-96-6	Dippr® 801 Database	C8H18O	130.2	179.8	71.1
2-ethylhexanol	104-76-7	Dippr® 801 Database	C8H18O	130.2	184.5	73.0
DIETHYLENE GLYCOL MONOETHYL ETHER	111-90-0	Sigma Aldrich MSDS	C6H13NO2	134.2	202.0	94.0
ETHYLENEGLYCOL PHENYL ETHER	122-99-6	Sigma Aldrich MSDS	C6H5OCH2CH2OH	138.0	247.0	121.0

Chemical Name	CAS	Reference	Chemical Formula	Mw	NBP, C	FP, C
DIETHYLENE GLYCOL MONOPROPYL ETHER	6881-94-3	Huntsman MSDS	C7H16O3	148.2	214.8	98.9
DIPROPYLENE GLYCOL MONOMETHYL ETHER	34590-94-8	Huntsman MSDS	C7H16O3	148.0	188.3	74.0
2-(2-(2-METHOXYETHOXY)ETHOXY)ETHANOL	112-35-6	Huntsman MSDS	C7H16O4	164.2	233.9	114.4
DiPropylene-Glycol-IsoPropyl-Ether	29911-27-1	Sigma Aldrich MSDS	C9H22O3	176.3	212.0	89.0
Neryl formate	2142-94-1	The Good Scent Company	C11 H18 O2	182.3	222.5	98.9
1-dodecanol	112-53-8	Dippr® 801 Database	C12H26O	186.3	264.0	124.9
ZF-10	83016-70-0	Huntsman MSDS	Proprietary	190.0	261.0	128.0
TRIPROPYLENE GLYCOL	24800-44-0	Huntsman MSDS	C9H20O4	192.0	270.5	140.0
SURFONIC L24-0.5	68551-12-2	Huntsman MSDS	Proprietary	194.3	281.1	138.0
2-(2-(2-BUTOXYETHOXY)ETHOXY)ETHANOL	143-22-6	Huntsman MSDS	C10H22O4	206.0	278.0	142.9
TRIPROPYLENE GLYCOL MONOMETHYL ETHER	25498-49-1	Dippr® 801 Database	C10H22O4	206.3	242.4	110.9
1-TETRADECANOL	112-72-1	Dippr® 801 Database	C14H30O	214.0	295.0	142.5
n-TRIDECANOIC ACID	638-53-9	Dippr® 801 Database	C13H26O2	214.0	312.4	164.9
NONYLPHENOL	25154-52-3	Dippr® 801 Database	C15H24O	220.2	317.6	157.9
1-PENTADECANOL	629-76-5	Dippr® 801 Database	C15H32O	228.2	310.8	150.9
SURFONIC L24-1.3	68551-12-2	Huntsman MSDS	Proprietary	229.4	291.0	149.0
TRIETHYLENE GLYCOL n-HEXYL ETHER	25961-89-1	Dippr® 801 Database	C12H26O4	234.2	296.6	150.9
n-PENTADECANOIC ACID	1002-84-2	Dippr® 801 Database	C15H30O2	238.2	337.5	180.9
TETRAETHYLENE GLYCOL MONOBUTYL ETHER	1559-34-8	Dippr® 801 Database	C12H26O5	250.2	304.3	162.8
1-HEPTADECANOL	1454-85-9	Huntsman MSDS	C17H36O	256.2	338.2	167.9
EMPILAN KA 2.5	66455-15-0	Huntsman MSDS	C16H34O3.5	282.2	301.2	150.0
OLEIC ACID	112-80-1	Dippr® 801 Database	C18H34O2	278.2	360.4	188.0
SURFONIC L24-2	68551-12-2	Huntsman MSDS	Proprietary	288.2	307.3	149.0
1-NONADECANOL	1454-84-8	Huntsman MSDS	C19H40O	284.2	362.0	184.9
SURFONIC SB-5	78330-20-8	Huntsman MSDS*	C16H34O4	290.2	306.8	149.0

Chemical Name	CAS	Reference	Chemical Formula	Mw	NBP, C	FP, C
1-EICOSANOL	629-96-9	Dippr® 801 Database	C20H42O	298.3	372.4	193.9
EMPILAN KBE 2.2/ PGL	68002-97-1	Huntsman MSDS	Proprietary	285.2	303.4	144.0
Surfonic L24-3	68551-12-2	Huntsman MSDS*	Proprietary	332.2	320.0	165.0
Surfonic L24-4	68551-12-2	Huntsman MSDS*	Proprietary	376.3	332.0	174.0
SURFONIC TDA-3B	24938-91-8	Huntsman MSDS	Proprietary	344.3	301.7	143.3
EMPIDERM B BASE	9003-13-8	Huntsman MSDS	Proprietary	393.3	287.4	136.0
Surfonic n-40	9016-45-9	Huntsman MSDS*	Proprietary	396.3	359.0	183.0
TERGITOL NP-4	9016-45-9	Dow chemical MSDS	C23H40O6	396.3	360.0	189.0
SURFONIC DNP-15	68891-21-4	Huntsman MSDS*	Proprietary	407.9	365.0	198.0
Surfonic L24-5	68551-12-2	Huntsman MSDS*	Proprietary	420.3	345.0	181.0
Surfonic T-5	61791-26-2	Huntsman MSDS*	Proprietary	511.4	358.0	190.0
Surfonic L24-7	68551-12-2	Huntsman MSDS*	Proprietary	508.4	364.0	191.0
Surfonic LSF23-9	67762-41-8	Huntsman MSDS*	Proprietary	589.4	376.0	195.0
SURFONIC L48-3	68213-23-0	Huntsman MSDS*	Proprietary	594.4	370.0	190.0
Surfonic P-3	68551-13-3	Huntsman MSDS*	Proprietary	632.5	382.4	204.0
SURFONIC N-100	9016-45-9	Huntsman MSDS*	Proprietary	660.4	396.3	213.0
SURFONIC LF-42	68439-51-0	Huntsman MSDS*	Proprietary	680.5	378.7	193.0
SURFONIC TDA-11	24938-91-8	Huntsman MSDS*	Proprietary	684.5	387.2	205.0
SURFONIC DDP-100	9014-92-0	Huntsman MSDS*	Proprietary	702.5	402.8	219.0
SURFONIC N-120	9016-45-9	Huntsman MSDS*	Proprietary	748.5	405.4	214.0
SURFONIC P5	68551-13-3	Huntsman MSDS*	Proprietary	769.3	389.4	206.0
Surfonic P-1	68551-13-3	Huntsman MSDS*	Proprietary	784.6	380.8	202.0
SURFONIC LPP L4-29XINT	9038-95-3	Huntsman MSDS*	Proprietary	828.6	376.7	196.0
Surfonic-OA15	68439-49-6	Huntsman MSDS*	Proprietary	930.6	408.2	226.7
PolyEthyleneGlycol-900	25322-68-3	Huntsman MSDS*	C40H82O21	898.5	415.6	226.0
SURFONIC DNP-140	68891-21-4	Huntsman MSDS*	Proprietary	961.7	420.4	229.0

Chemical Name	CAS	Reference	Chemical Formula	Mw	NBP, C	FP, C
JEFFOX WL 590	9082-00-2	Huntsman MSDS*	Proprietary	985.6	425.8	236.0
SURFONIC LF-41	68891-11-2	Huntsman MSDS*	Proprietary	998.7	415.5	215.0
SURFONIC LF-37	68154-97-2	Huntsman MSDS*	Proprietary	1075.7	396.9	218.0
Surfonic n-200	9016-45-9	Huntsman MSDS*	Proprietary	1100.7	429.2	232.3
SURFONIC L24-22	9016-45-9	Huntsman MSDS*	Proprietary	1168.7	425.2	233.6
POGOL-VP1100	126682-74-4	Huntsman MSDS*	Proprietary	1107.7	424.5	238.0
TERGITOL™ NP-40 Surfactant	9016-45-9	Dow chemical MSDS*	C95H184O41	1981.2	463.6	257.0
SURFONIC N-400	9016-45-9	Huntsman MSDS*	Proprietary	1981.2	463.6	250.0
XTF912	9063-06-3	Huntsman MSDS*	Proprietary	2118.3	448.3	234.3
PED 2003	9001-11-5	Huntsman MSDS*	Proprietary	1974.2	455.6	238.0
SURFONIC POA-L62	9003-11-6	Huntsman MSDS*	Proprietary	2193.4	433.4	225.0
JEFFOX WL 1400	9003-11-6	Huntsman MSDS*	Proprietary	2195.7	455.8	246.0

*Reference gives experimental flash point value but normal boiling point is estimated by equation (39)

Table A3 Test data set for flash point method; non-OH and non-amide containing compounds

Chemical Name	CAS	Reference	Chemical Formula	Mw	NBP, C	FP, C
diethylenetriamine	111-40-0	Dippr® 801 Database	C4H13N3	103.0	207.0	95.0
JEFFAMINE® EDR-104 Etheramine	2752-17-2	Huntsman MSDS	Proprietary	104.0	198.0	90.0
NEOPENTANEDIAMINE	7328-91-8	Sigma Aldrich MSDS	C5H14N2	102.0	153.0	47.0
o-Toluidine	95-53-4	Dippr® 801 Database	C7H9N	107.2	200.3	85.0
cyclohexanemethylamine	3218-02-8-	Sigma Aldrich MSDS	C7H15N	113.0	160.0	48.0
1,4-dimethylpiperazine	106-58-1	Dippr® 801 Database	C6H14N2	114.0	131.0	21.5
2,4-dimethylaniline	95-68-1	Dippr® 801 Database	C8H11N	121.0	218.0	98.0
N,N-dimethylaniline	121-69-7	Dippr® 801 Database	C8H11N	121.0	193.5	75.0
n-NonylAmine	112-20-9	Dippr® 801 Database	C9H21N	143.3	202.7	74.0
DIETHYLENE GLYCOL DIMETHYL ETHER	111-96-6	Dippr® 801 Database	C6H14O3	134.0	162.5	62.8
1-METHYLNAPHTHALENE	90-12-0	Dippr® 801 Database	C11H10	142.0	244.7	92.0
Triethylenetetramine	112-24-3	Dippr® 801 Database	C6H18N4	146.3	266.5	135.0
XTJ-504	929-59-9	Huntsman MSDS	Proprietary	148.0	251.0	129.0
(E,Z)-2,4-decadien-1-al	25152-84-5	The Good Scent Company	C10 H16 O	152.2	246.0	101.5
aldehydic nitrile	40188-41-8	The Good Scent Company	C10 H19 N	153.0	223.0	88.0
Tetramethylbis(aminoethyl)ether	3033-62-3	Huntsman MSDS	C8H20NO	160.0	189.0	69.0
DIETHYLENE GLYCOL DIETHYL ETHER	112-36-7	Huntsman MSDS	C8H18O3	162.0	189.0	82.0
octanal dimethyl acetal	54889-48-4	The Good Scent Company	C10 H22 O2	174.3	186.5	68.3
DIPROPYLENE GLYCOL n-BUTYL ETHER	29911-28-2	Huntsman MSDS	C10H22O3	190.0	231.7	100.4
1-n-PROPYLNAPHTHALENE	2765-18-6	Huntsman MSDS	C13H15	171.0	272.8	113.9
TRI-n-BUTYL PHOSPHATE	126-73-8	Dippr® 801 Database	C12H27O4P	266.3	289.0	134.9
PMDETA	3030-47-5	Huntsman MSDS	C9N3H23	173.2	215.0	93.0
DIETHYLENE GLYCOL ETHYL ETHER ACETATE	112-15-2	Huntsman MSDS	C8H16O4	176.0	217.4	96.0
(E)-2-nonen-1-yl acetate	30418-89-4	The Good Scent Company	C11H20O2	184.3	236.0	98.0
DI-n-HEXYL ETHER	112-58-3	Huntsman MSDS	C12H26O	186.0	225.7	78.0

Chemical Name	CAS	Reference	Chemical Formula	Mw	NBP, C	FP, C
decanal dimethyl acetal	34764-02-8	The Good Scent Company	C12H26O2	202.3	238.0	93.0
TRI-o-CRESYL PHOSPHATE	78-30-8	Dippr® 801 Database	C21H21O4P	369.0	410.0	225.0
m-Terphenyl	92-06-8	Dippr® 801 Database	C18H14	230.0	372.0	190.9
DI-2-ETHYLHEXYLAMINE	106-20-7	Dippr® 801 Database	C16H35N	241.5	281.0	131.9
METHYL OLEATE	112-62-9	Dippr® 801 Database	C19H36O2	296.5	344.0	176.9
DI-n-OCTYL ETHER	629-82-3	Dippr® 801 Database	C16H34O	242.2	286.5	138.9
DMDEE	6425-39-4	Huntsman MSDS	C12H24N2O3	244.2	299.0	153.0
hexadecane	544-76-3	Dippr® 801 Database	C16H34	226.2	287.0	135.0
TRIPHENYL PHOSPHATE	115-86-6	Dippr® 801 Database	C18H15O4P	326.3	413.5	220.0
1-n-NONYLNAPHTHALENE	26438-26-6	Dippr® 801 Database	C19H26	254.2	366.0	185.9
DINONYL ETHER	2456-27-1	Dippr® 801 Database	C18H38O	270.2	317.9	156.9
Surfonamine B-30	No CAS#	Huntsman MSDS*	Proprietary	321.4	318.0	159.5
XTJ-507	83713-01-3	Huntsman MSDS*	Proprietary	1966.3	417.0	210.0
JEFFAMINE M 2070	83713-01-3	Huntsman MSDS*	Proprietary	1976.2	444.0	243.0
JEFFAMINE D-2000	9046-10-0	Huntsman MSDS*	Proprietary	1989.3	420.0	215.0

*Reference gives experimental flash point value but normal boiling point is estimated by equation (39)

Table A4 Test data set for flash point method; -OH and amide containing compounds

Chemical Name	CAS	Reference	Chemical Formula	Mw	NBP, C	FP, C
2,5-hexanediol	2935-44-6	Sigma Aldrich MSDS	C6H14O2	118.0	217.0	101.0
ETHYLENEGLYCOL MONOBUTYL ETHER	111-76-2	Sigma Aldrich MSDS	C4H14O2	118.0	171.0	65.0
2,3-dimethyl-2,3-butanediol	76-09-5	Sigma Aldrich MSDS	C6H14O2	118.0	171.0	77.0
DIISOPROPANOLAMINE	110-97-4	Huntsman MSDS	C6H15NO2	133.0	248.8	135.0
n-HEXANOIC ACID	142-62-1	Dippr® 801 Database	C6H12O2	116.0	205.7	102.0
Monomethylethanolamine	109-83-1	Dippr® 801 Database	C3H9NO	75.1	158.0	72.0
2-(2-(2-ETHOXYETHOXY)ETHOXY)ETHANOL	112-50-5	Dippr® 801 Database	C8H18O4	178.0	256.0	135.0
SURFONIC OP-15	9036-19-5	Huntsman MSDS	Proprietary	271.4	329.8	163.0
DIISOPROPANOLAMINE	110-97-4	Dippr® 801 Database	C6H14NO2	132.0	248.8	123.9
2-(2-ETHOXYETHOXY)ETHANOL	111-90-0	Dippr® 801 Database	C6H14O3	134.0	201.9	83.3
Triethanolamine	102-71-6	Dippr® 801 Database	C6H15NO3	149.2	335.4	179.9
DIETHYLENEGLYCOL METHYL ETHER	111-77-3	Sigma Aldrich MSDS	C5H12O3	120.0	193.0	85.0
TETRAHYDROFURFURYL ALCOHOL	97-99-4	Dippr® 801 Database	C5H10O2	102.0	177.7	70.0
N,N-diMethyldiGlycolAmine	1704-62-7	Sigma Aldrich MSDS	C6H15NO2	133.2	204.8	93.0
DMDGA N,N-dimethyl-2(2-aminoethoxy)ethanol (ZR-70)	1704-62-7	Huntsman MSDS	C8O2H15N	133.2	201.0	97.0
6-AMINOHEXANAMIDE	1704-62-7	Dippr® 801 Database	C6H14N2O	130.0	308.3	170.9
2-ETHYL-1-HEXANOL	104-76-7	Dippr® 801 Database	C8H18O	130.0	184.6	72.9
2-(2-BUTOXYETHOXY)ETHANOL	112-34-5	Dippr® 801 Database	C8H18O3	146.0	231.0	100.0
2-HEXOXYETHANOL	112-25-4	Dippr® 801 Database	C8H18O2	146.2	208.3	81.9
TRIETHYLENE GLYCOL	112-27-6	Dippr® 801 Database	C6H14O4	150.0	278.0	155.0
Ethylene-Glycol-2-EthylHexyl-Ether	1559-35-9	Dippr® 801 Database	C10H22O2	174.3	227.6	109.0
2-(2-HEXOXYETHOXY)ETHANOL	112-59-4	Dippr® 801 Database	C10H22O3	190.0	259.1	135.0
TETRAETHYLENE GLYCOL	112-60-7	Dippr® 801 Database	C8H18O5	194.0	329.6	195.9
2-BUTYL-NONAN-1-OL	51655-57-3	Dippr® 801 Database	C13H28O	200.0	264.9	133.9

Chemical Name	CAS	Reference	Chemical Formula	Mw	NBP, C	FP, C
TRIPROPYLENE GLYCOL MONOETHYL ETHER	75899-69-3	Dippr® 801 Database	C11H24O4	220.3	251.8	131.9
p-tert-OCTYLPHENOL	140-66-9	Dippr® 801 Database	C14H22O	206.0	290.5	136.9
TRIPROPYLENE GLYCOL MONOMETHYL ETHER	25498-49-1	Dippr® 801 Database	C10H22O4	206.0	242.4	110.9
p-CUMYLPHENOL	599-64-4	Dippr® 801 Database	C15H16O	212.0	335.0	170.9
n-OCTADECANOIC ACID	57-11-4	Dippr® 801 Database	C18H36O2	284.0	374.0	193.1
SURFONIC L12-2.6	66455-15-0	Huntsman MSDS*	Proprietary	286.4	291.9	136.0
EMPILAN KBE 3	68002-97-1	Huntsman MSDS*	Proprietary	343.0	321.5	175.0
n-NONADECANOIC ACID	646-30-0	Dippr® 801 Database	C19H38O2	298.0	384.0	190.3
PIMARIC ACID	127-27-5	Dippr® 801 Database	C20H30O2	302.0	350.0	173.5
SURFONIC L12-3	66455-15-0	Huntsman MSDS*	Proprietary	304.2	297.8	138.0
PolyEthyleneGlycol-400	25322-68-3	Huntsman MSDS*	Proprietary	418.6	364.9	199.0
SURFONIC POA-L62LF	9003-11-6-	Huntsman MSDS*	Proprietary	2244.2	434.1	231.0
SURFONIC L12-8	66455-15-0	Huntsman MSDS*	Proprietary	509.3	363.2	175.5
Surfonic P-5	68551-13-3	Huntsman MSDS*	Proprietary	769.3	395.3	226.7
Surfonic OP-50	9036-19-5	Huntsman MSDS*	Proprietary	426.3	365.0	187.8
Surfonic OP-100	9036-19-5	Huntsman MSDS*	Proprietary	646.4	396.0	229.0
SURFONIC TDA-8	24938-91-8	Huntsman MSDS*	Proprietary	552.4	366.5	178
Surfonic P-3	68551-13-3	Huntsman MSDS*	Proprietary	632.4	376.0	214.4
Surfonic P-6	68987-81-5	Huntsman MSDS*	Proprietary	1877.2	425.0	223.9
SURFONIC L12-6	66455-15-0	Huntsman MSDS*	Proprietary	424.3	346.7	164.8
Surfonic n-60	9016-45-9	Huntsman MSDS*	Proprietary	484.3	383.0	221.0
SURFONIC L24-22	68551-12-2	Huntsman MSDS*	Proprietary	1168.7	428.0	233.6
SURFONIC N-150	9016-45-9	Huntsman MSDS*	Proprietary	880.6	415.2	236.8
JEFFOX WL 5000	9038-95-3	Huntsman MSDS*	Proprietary	4105.5	469.5	237.5
PolyEthyleneGlycol-1450	25322-68-3	Huntsman MSDS*	Proprietary	1426.8	444.0	229.0
PolyEthyleneGlycol-600	25322-68-3	Huntsman MSDS*	Proprietary	616.7	395.0	214.5

Chemical Name	CAS	Reference	Chemical Formula	Mw	NBP, C	FP, C
Surfonic-T-15	61791-26-2	Huntsman MSDS*	Proprietary	928.6	415.0	231.0
Surfonic T-10	61791-26-2	Huntsman MSDS*	Proprietary	709.5	393.0	214.5
Jeffox OL300	9003-13-8	Huntsman MSDS*	Proprietary	1645.2	388.2	188.0
Jeffox OL460	9038-95-3	Huntsman MSDS*	Proprietary	1963.4	402.0	196.1
Surfonic T-2	61791-26-2	Huntsman MSDS*	Proprietary	357.3	323.0	150.0
SURFONIC L24-12	68551-12-2	Huntsman MSDS*	Proprietary	728.5	391.0	204.0
SURFONIC LF-37	68154-97-2	Huntsman MSDS*	Proprietary	1075.7	391.5	191.7
SURFONIC POA-L61	9003-11-6-	Huntsman MSDS*	Proprietary	2105.4	426.3	229.0
SURFONIC LF-110	68439-30-5	Huntsman MSDS*	Proprietary	1144.3	401.0	219.0

*Reference gives experimental flash point value but normal boiling point is estimated by equation (39)

APPENDIX B

Table B1 Training dataset for development of normal boiling point prediction method

Name	CAS#	Mw	NBP, C	Weight
tri-n-PropylAmine	102-69-2	143.27	156.51	1.00
p-Cresol	106-44-5	108.14	201.97	1.00
Ethylene-Glycol-MonoPropyl-Ether	2807-30-9	104.15	150.04	1.00
Phenol	108-95-2	94.11	181.89	1.00
Thancat-ZF20	3033-62-3	160.26	188.93	0.50
p-diIsoPropylBenzene	100-18-5	162.27	210.18	1.00
N,N-diEthylEthanolAmine	100-37-8	117.19	161.95	1.00
2-ButoxyEthanol	111-76-2	118.18	170.49	1.00
2,2-MethoxyEthoxy-Ethanol	111-77-3	120.15	193.98	1.00
MethoxyEthylMorpholine	10220-23-2	145.20	192.58	1.00
o-Xylene	95-47-6	106.17	144.42	1.00
Jeffcat-LE-60	65573-13-9	146.23	202.12	1.00
N-HydroxyEthylMorpholine	622-40-2	131.17	224.68	0.65
p-Phenetidine	156-43-4	137.18	248.59	1.00
n-NonylAmine	112-20-9	143.27	202.66	1.00
N,N-diMethyldiGlycolAmine	1704-62-7	133.19	204.77	0.90
p-AminoPhenol	123-30-8	109.13	268.63	0.01
2,2-EthoxyEthoxy-Ethanol	111-90-0	134.18	201.63	1.00
N-EthylAniline	103-69-5	121.18	204.60	1.00
N-AminoEthyl-Piperazine	140-31-8	129.20	221.83	1.00
triButylAmine	102-82-9	185.35	213.94	1.00
XTJ564	No CAS#	119.16	233.09	1.00
PentaMethylBenzene	700-12-9	148.25	231.67	1.00

Name	CAS#	Mw	NBP, C	Weight
N-EthylDGA	106007-99-2	133.19	221.67	1.00
N-AminoEthyl-EthanolAmine	111-41-1	104.15	243.37	1.00
2-HexyloxyEthanol	112-25-4	146.23	207.33	1.00
1,1-diPhenylEthane	612-00-0	182.26	270.92	0.50
o-Toluidine	95-53-4	107.15	200.34	1.00
p-tert-AmylPhenol	80-46-6	164.25	266.49	1.00
tetraMethyltriEthyleneGlycol diAmine	3065-46-1	204.31	243.52	0.50
Jeffcat-ZR50b	6711-48-4	187.33	235.37	0.30
diEthylene-Glycol	111-46-6	106.12	245.09	1.00
N-Methyl-N-(3-AminoPropyl)EthanolAmine	41999-70-6	132.21	236.83	1.00
triEthyleneglycolmonoMethylEther	112-35-6	164.20	249.62	0.61
Methyl-diEthanolAmine	105-59-9	119.16	246.96	1.00
Ethylene-Glycol-2-EthylHexyl-Ether	1559-35-9	174.28	227.65	1.00
triEthylene-Glycol-MonoAmine	6338-55-2	149.19	270.88	0.79
doDecylAmine	124-22-1	185.35	258.78	1.00
diEthanolAmine	111-42-2	105.14	269.44	0.55
triEthyleneglycolmonoEthylEther	112-50-5	178.23	249.70	0.33
1,2,3,5-tetraEthylBenzene	38842-05-6	190.33	248.14	1.00
tetraEthylene-Glycol-diMethyl-Ether	143-24-8	222.28	275.75	1.00
2-{2-((2-HydroxyEthyl)MethylAmino) Ethoxy}Ethan-1-ol	68213-98-9	163.22	288.37	0.47
triEthylene-tetraAmine	112-24-3	146.24	275.41	0.76
Jeffcat-ZF10	83016-70-0	190.29	262.96	0.98
1,2,3-ButaneTriol	4435-50-1	106.12	264.66	0.50
BAEE-EO	No CAS#	148.20	279.19	0.24
triPropylene-Glycol-Ethyl-Ether	75899-69-3	220.31	246.23	0.50

Name	CAS#	Mw	NBP, C	Weight
2-(2-HexyloxyEthoxy)Ethanol	112-59-4	190.28	257.95	0.50
triEthylene-Glycol	112-27-6	150.17	288.83	0.51
triPropylene-Glycol	24800-44-0	192.25	270.30	0.59
1-tetraDecanAmine	2016-42-4	213.41	291.52	1.00
p-TerPhenyl	92-94-4	230.31	383.85	1.00
triEthyleneglycolmonoButylEther	143-22-6	206.28	278.83	0.28
N-HydroxyEthyl-DETA	1965-29-3	147.22	303.00	0.35
Jeffcat-ZR50	67151-63-7	245.41	320.67	0.08
Jeffcat-DPA	63469-23-8	218.34	267.57	0.31
N-AminoPropyldiEthanolAmine	4985-85-7	162.23	325.96	0.14
tetraEthylene-Glycol	112-60-7	194.23	326.96	0.15
tetraEthylenePentaAmine	112-57-2	189.30	327.05	0.20
triEthanolAmine	102-71-6	149.19	335.21	0.45
tetraPropyleneglycol	25657-08-3	250.33	306.82	0.23
NonylPhenol	25154-52-3	220.35	302.89	0.37
Surfonic-C300	176022-81-4	329.17	327.38	0.06
PentaEthyleneHexylAmine	4067-16-7	232.37	376.38	0.14
1,1,4,6-tetraMethylIndane	941-60-6	174.29	234.09	0.38
1,1-di(4-Tolyl)-Ethane	530-45-0	210.32	298.04	1.00
1,3-diMethoxyBenzene	151-10-0	138.17	224.04	1.00
1-AzaCycloOctane	1121-92-2	113.20	156.55	0.01
1-CycloHexylAmino-2-Propanol	103-00-4	157.26	238.06	1.00
2-(2-biPhenylyoxy)-Ethanol	7501-02-2-	214.26	334.07	0.22
2,4"-diAmino-diPhenylMethane	1208-52-2	198.27	383.16	0.01
2,4,5-triMethyl-BenzenAmine	137-17-7	135.21	225.89	0.52
2-AnilinoEthanol	122-98-5	137.18	279.37	1.00

Name	CAS#	Mw	NBP, C	Weight
4-(ButylAmino)-Phenol	103-62-8	165.23	300.50	0.08
4,4"-diAmino-diPhenylMethane	101-77-9	198.27	376.20	0.03
AEEAEO	4439-20-7	148.20	315.79	0.11
AminoEthoxyEthylMorpholine	61565-39-7	174.24	260.85	0.68
bis-diAminodiPropyl-EthylenediAmine	63833-76-1	288.48	367.21	0.02
bis-N,N-(2-Hydroxy-3-PhenOxyPropyl)-PhenylAmine	3088-05-9	393.48	439.00	0.01
diTEG-triAmine	50977-95-2	279.38	334.62	0.06
Empilan-KBE1	68002-97-1	238.81	296.66	0.28
Empilan-KBE2.2	68002-97-1	291.67	307.00	0.22
Ethylene-Glycol-diIsoButyl-Ether	5669-09-0	174.28	181.58	1.00
Ethylene-Glycol-monoBenzyl-Ether	622-08-2	152.19	255.56	1.00
Ethylene-Glycol-monoIsoPropyl-Ether	109-59-1	104.15	141.63	1.00
GP300	25791-96-2	300.60	329.24	0.02
JeffAmine-C346	102344-00-3	405.21	366.62	0.05
JeffAmine-D230	9046-10-0	225.96	265.50	0.79
JeffAmine-ED220	194673-87-5	220.31	272.53	0.44
JeffAmine-EDR192	929-75-9	192.26	297.14	0.43
JeffAmine-M360	70914-41-9	367.53	359.25	0.08
JeffAmine-PM600-Intermediate	9063-06-3-	228.31	239.17	0.25
Jefflink-754	156105-38-3	254.46	269.33	0.30
Jeffol-A31-600-ARL1	35176-06-8	279.38	359.92	0.24
Jeffol-A480	25214-63-5	466.66	358.10	0.02
Jeffol-A630	37208-53-0	294.39	331.84	0.02
Jeffol-A770	25214-63-5	292.42	373.09	0.03
Jeffol-G30-650	25791-96-2	260.53	355.76	0.12

Name	CAS#	Mw	NBP, C	Weight
MethoxyPropylMorpholine	82057-89-4	159.23	211.28	1.00
N,N,2-triMethyl-BenzenAmine	609-72-3	135.21	177.40	0.03
N,N,N"-TriMethyl-N"-(2-HydroxyEthyl)-1,2-EthanediAmine	2212-32-0	146.23	206.66	0.24
N,N-bis(2-HydroxyEthyl)Aniline	120-07-0	181.23	337.83	1.00
N,N-diEthyl-diGlycolAmine	140-82-9	161.24	223.55	1.00
N-Ethyl-bis(AminoEthyl)Ether	30336-23-2	132.21	195.56	1.00
N-EthyldiEthylenetriAmine	24426-14-0	131.22	214.53	0.83
N-HydroxyEthyl-DGA	5038-17-5	149.19	321.55	0.20
N-Methyl-1-OctanAmine	2439-54-5	143.27	186.00	1.00
N-MethylIminobisPropylAmine	105-83-9	145.25	233.76	1.00
p-(1-Methyl-1-EthylPentyl)Phenol	1988-35-8	206.33	293.68	1.00
PED220	132435-10-0	222.28	299.11	0.28
PentaMethyldiEthylenetriAmine	3030-47-5	173.30	203.12	1.00
PentaMethyldiPropylenetriAmine	3855-32-1	198.35	239.07	1.00
PolyEthyleneGlycol-150	25322-68-3	150.17	271.22	0.15
PolyEthyleneGlycol-200	25322-68-3	216.25	317.70	0.26
Polyol-PC300	176022-76-7	328.14	341.32	0.06
Polyol-PM272	9063-06-3-	268.34	256.00	0.12
PolyPropyleneGlycol-150	25322-69-4	150.44	271.47	0.15
PolyPropyleneGlycol-230	25322-69-4	232.91	285.82	0.55
Propyl-Phenyl-Ether	622-85-5	136.19	189.80	0.50
PXTJ568	No CAS#	213.49	286.28	0.53
Safol-L23-2	66455-14-9	274.46	306.00	0.31
Safol-L23-3	66455-14-9	325.51	346.00	0.17
Surfol-610L	37311-02-7	304.47	292.72	0.05

Name	CAS#	Mw	NBP, C	Weight
Surfonic-ADA100	413850-70-3	292.42	365.00	0.01
Surfonic-DA4	78330-20-8	338.90	281.83	0.48
Surfonic-DDA3	78330-21-9	318.50	293.77	0.10
Surfonic-DDA6	78330-21-9	450.65	349.78	0.14
Surfonic-DNP15	68891-21-4	408.27	385.51	0.12
Surfonic-DNP40	68891-21-4	522.81	375.54	0.07
Surfonic-EH2	71060-57-6	218.34	235.79	1.00
Surfonic-EH9	26468-86-0	526.71	349.93	0.11
Surfonic-L10-3	68439-45-2	290.44	293.74	0.22
Surfonic-L12-2.5	66455-15-0	282.44	275.00	0.36
Surfonic-L12-3	66455-15-0	304.47	297.83	0.44
Surfonic-L12-5	66455-15-0	392.58	330.00	0.12
Surfonic-L1270-2	68551-12-2	282.86	311.92	0.58
Surfonic-L24-0.5	68551-12-2	216.78	281.14	0.76
Surfonic-L24-1	68551-12-2	238.81	289.81	0.39
Surfonic-L24-2	68551-12-2	283.70	306.41	0.18
Surfonic-L610-3	68439-45-2	262.39	279.97	0.43
Surfonic-L6-3.9	31726-34-8	273.98	285.70	0.66
Surfonic-L810-4.5	68439-45-2	360.12	306.09	0.22
Surfonic-N10	9016-45-9	264.41	346.74	0.04
Surfonic-OP15	9036-19-5	272.41	329.81	0.03
Surfonic-SB5	78330-20-8	293.25	268.00	0.02
Surfonic-T5	61791-26-2	489.78	393.32	0.01
Surfonic-TDA3	24938-91-8	332.52	322.09	0.18
TEA-EO	17626-34-5	193.24	358.46	0.02
Teric-407	9003-13-8	306.44	253.75	0.15

Name	CAS#	Mw	NBP, C	Weight
tetraEGMA	86770-74-3	193.24	317.27	0.24
tetrakis(2-HydroxyPropyl)EthylenediAmine	102-60-3	292.42	373.10	0.17
tetraPropylene-Glycol-MonoIsoPropyl-Ether	No CAS#	292.41	292.40	0.50
Thancat-DD	34745-96-5	174.29	206.38	0.96
triEthylene-Glycol-diAmine	929-59-9	148.20	246.45	1.00
tri-IsoPropanolAmine	122-20-3	191.27	308.12	0.90
Triol-T400	25723-16-4	401.34	367.22	0.01
triPropylene-Glycol-Butyl-Ether	57499-93-1	248.36	269.57	0.50
triPropyleneglycoldiAmine	26392-60-9	190.29	247.12	0.65
triPropylene-Glycol-Methyl-Ether	20324-33-8	206.28	241.25	0.50
triPropylene-Glycol-MonoIsoPropyl-Ether	No CAS#	234.34	256.73	1.00
triPropylenetetraAmine	31511-99-6	188.32	298.12	0.07
XTJ566	No CAS#	391.59	366.00	0.04
XTJ568	No CAS#	215.34	279.96	0.63
XTJ584	No CAS#	302.50	293.71	1.00

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